



Courtesy B. F. Goodrich Co.

Solvent Recovery Unit at Koroseal Plant

What is believed to be the largest solvent recovery unit in the United States is being operated by The B. F. Goodrich Co. at its recently opened Koroseal spreading plant. The photograph shows the three towers comprising the unit. The largest, right, is 10 feet in diameter, 78 feet high, and weighs 130,000 pounds. The center is 6 feet, 6 inches in diameter, 68 feet high, and 51,000 pounds in weight, while the smallest is 2 feet, 6 inches in diameter, 54 feet high, and weighs 12,000 pounds. All the towers were received on the site completely assembled and were erected in one piece.

THE RECOVERY OF VAPORS

WITH SPECIAL REFERENCE
TO VOLATILE SOLVENTS

by

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Preface

Twenty years ago there appeared a book by the author entitled *The Recovery of Volatile Solvents*. Since that time there have been two French editions of that book, the English edition being long out of print. Interest in the subject has grown very considerably since then, not only in volatile solvents but also in the problems connected with the recovery of other industrial vapors not strictly in the class of solvents. The present book is an attempt to bring the subject matter of the earlier book up to date and in addition to include other material in the wider field of vapors in general.

The commercial recovery of vapors is of relatively recent origin. This is due to a number of reasons. In the first place the industries making use of solvents in large amounts have been until recently of limited extent both as to numbers and as to size; and in the second place, the increasing cost of the solvents themselves as well as their increasing scarcity in many cases has only in the last few decades forced industry to attempt their recovery. There have also arisen new fields in which the same methods of recovery can be applied, such as the recovery of natural gasoline from natural gas, the recovery of alcohol vapor from the gases liberated in the fermentation of sugars, the removal of water vapor from air and other gases in various industries, and many other examples of great industrial importance. This increased interest in a rapidly widening subject is responsible for this book.

The recovery of vapors does not involve any new principles with which the skilled chemical engineer is unfamiliar and anyone well trained along chemical engineering lines will find that a considerable portion of this book, at the start at least, consists of the most

elementary principles of chemical engineering. In his experience as a consultant on chemical engineering equipment, the author has frequently found it necessary to give his clients a fairly complete course in the basic principles underlying the operation of the equipment under discussion, and he has found by experience that the method of presentation used in this book is most advantageous. It has therefore been the object of the author to present in as simple and complete form as possible the fundamental principles involved in the recovery of vapors, illustrating them with numerous examples, to discuss briefly the various factors entering into the design of recovery equipment, and to give descriptions of the standard forms of apparatus in more common use.

There are two phases of the greatest importance in the operation of solvent recovery plants in particular which the author has practically omitted from this book, namely, the evaporation of the solvent from the material in which it has been used and the subsequent fractional distillation of the recovered solvent to separate it from the absorbing liquid or other substances present and to purify it for reuse. There are two reasons for this. In the first place both of these phases are specialized operations of the first magnitude, deserving separate treatises of considerable length, the brief treatment possible in a book of this size being of no value. And in the second place both of these subjects have already been covered in other books that are readily available to all. For those interested in the basic principles of vaporization as applied to the removal of the solvent from the material with which it is associated, the author recommends the "Principles of Chemical Engineering," third edition, by Walker, Lewis, McAdams and Gilliland. For the subsequent purification and separation for reuse of the recovered solvents, the reader is referred to the "Elements of Fractional Distillation," third edition, by Robinson and Gilliland.

The picture in regard to the recovery of vapors has changed considerably in the past twenty years. The use of solid adsorbents such as silica gel, activated alumina and particularly activated carbon has grown more rapidly than the use of some of the older methods. Furthermore, a great number of new solvents have appeared on the market due to the advances in synthetic organic chemistry and to the increased demand by users of lacquers, resins, plastics and the like for solvents of very special properties. And perhaps most important of all, the necessity for reducing the fire risk, the dangers of industrial poisoning, and the need for lowering manufacturing costs have made the proper handling of solvent vapors of the greatest importance.

This book is not a reference book nor is it a complete treatise on the subject, but rather it is a course of study in the basic theory of the recovery of vapors for the benefit of engineers and others who find that they need elementary information on the subject. The reader is expected to start at the beginning and read the contents approximately consecutively if he is to obtain a fair grasp of the subject. It is obviously not meant for the expert in the field but rather for the beginner who wants to enter it.

The author is indebted to a large number of firms and individuals for material which has been used in the book. Credit is given in the text for the material as used and it is hoped that there have been no omissions. It will be much appreciated if errors of omission or commission are called to the author's attention.

The author is particularly indebted to Dr. A. B. Ray of the Carbide and Carbon Chemicals Corporation of New York who has read the manuscript and made numerous suggestions, many of which have been adopted. He has pointed out that many of the older methods for solvent recovery described in this book have been rendered obsolete by the use of activated carbon and that undue space has been devoted to them

on that account. The author pleads guilty to this and offers as his excuse for including them his conviction that a description of the early art helps to explain present practice, particularly when the methods in question have considerable theoretical interest. Mr. E. L. Luaces of Dayton, Ohio has also been most helpful in criticizing portions of the book.

The literature on the recovery of vapors has grown to enormous size in the past few years and it is suggested that those interested in carrying the study of the subject further than is done in this book refer to the *Chemical Abstracts* of the American Chemical Society which is available in most large libraries and at all technical schools. The listing in *Chemical Abstracts* is very complete and easy to use.

Finally the author wishes to say that in all his consulting experience in the field of the recovery of vapors, no two problems were alike, and that the solution in every case was different from every other solution. It is necessary to treat each problem on its own merits, basing the solution on the experience gained in previous work, tempered by a proper application of chemical engineering principles.

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Cambridge, Mass.

February 1, 1942

The text of this book was edited by Lillian Hall Jenkins and most of the diagrams were drawn by Harry J. Heineman, Jr.

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Chapter 1

Introduction

Solvents, in the sense used in this book, are those substances, usually volatile liquids, which are added to materials for the purpose of temporarily changing their physical properties so that they can be more readily used in manufacturing processes, or for application in their particular use. When this is finished, the solvents are then wholly or partially removed, either by a special solvent removal process, such as artificial drying, or by a natural process such as evaporation into the air. For example, the solvents used in paints and varnishes are added in order to change a pasty or gummy material to the fluid state so that it can be applied by brush or sprayer, or by dipping. The solvent, which is volatile, is then allowed to evaporate, either into the open air, where it is lost, or in a suitable drier where it can be recovered for reuse. Another example is the addition of a mixture of solvents to nitrocellulose when it is in the form of nitrated cotton fibers, so that a plastic mass is formed which can be moulded into desired shapes. The volatile portion of these solvents is subsequently removed in a specially designed drier which returns the dissolved material to the solid state, and the vaporized solvent is recovered or lost as the case may be.

The commonest solvent, water, is rarely recovered from drying processes for reuse. Most of the other solvents in common use are liquids of organic origin, either obtained from natural sources or made synthetically, and are relatively costly as compared with water. When used in large quantities it may be necessary to recover them for economic reasons or because of the limited supply of solvent available. Also, the possible inflam-

mable or poisonous nature of the vaporized solvent may make it advisable to recover it to reduce the risk involved.

Once that it has been decided to attempt to recover the vaporized solvent, the problem becomes one of selecting the best method of doing so. In general, there are three methods, and they may be used singly or in combination. The first method consists of cooling the mixture of solvent vapor and gas with which it is associated to below its solvent dew point so that the solvent will partly condense and may be separated and removed. The second is the use of some relatively less volatile liquid in which the solvent is soluble, bringing the gaseous mixture containing the solvent into contact with such a liquid so that some of the solvent will be dissolved by it, and subsequently separating the two materials by fractional distillation. The third method makes use of the property of certain solid substances of adsorbing or condensing on their surfaces the vapor in question. The adsorbed vapor is afterwards removed by high-temperature vaporization, usually with the aid of steam. Which one of these three methods or what combination of them is best for a particular case must be determined by investigation.

The factors which enter into the selection of the best method for recovering the solvent in a particular case are several. The first and perhaps most important is the value of the recovered solvent. Ethyl alcohol, gasoline fractions, and benzene, for example, are relatively low-priced solvents, while chlorinated hydrocarbons such as trichloroethylene, esters such as the acetates of the fatty acids, and synthetically prepared esters and ketones are much more costly and represent a substantial economic factor. But, regardless of the cost of the solvent, it may be so difficult to recover it in its original condition that the cost involved in so doing may make such recovery inadvisable. The incentive to recover the higher-priced solvents is of course greater,

and it is usually feasible to make the necessary expenditure for equipment essential in reclaiming them.

Also, the risk involved in permitting the solvent vapor to escape into the air may necessitate recovery of the solvent, even at an economic loss.

Most solvents form explosive mixtures with air. Fortunately for any particular solvent, there are upper and lower limits to the percentage of solvent vapor which must be present in order to constitute an explosive mixture, the value of the limits depending on the temperature and pressure of the mixture. If the mixture of the solvent vapor and the air lies outside these limits, there can be no explosion and it is safe to handle. For many solvents at room temperature and ordinary pressures, these limits lie between 1.0 and 10.0 per cent of solvent vapor by volume. On this account, safety demands that the recovery process be operated always outside of these limits, and preferably below. Plants which have failed to observe this rule have sooner or later had disastrous results, not only to the factory but to the vicinity at large, as the explosion of solvent equipment of any size is almost sure to wreck everything within a considerable radius. Occasionally, the requirements of the process make it necessary to operate within the explosive limits. Under these conditions, the only safe procedure is to use enclosed equipment and have no air present. This is easily achieved by substituting inert gases for air. An example of this is the Lewis Process, which uses washed, oxygen-free flue-gas instead of air. Or if the equipment will permit, other gases may be dispensed with, and vacuum or pressure substituted to permit the vaporization and subsequent condensation of the solvent. It is an interesting fact that explosions of solvent-air mixtures are most violent when near the lower explosive limit and that the violence decreases as the percentage of the vapor rises, until at the upper limit, the explosion is hardly noticeable.

There are certain general rules in regard to the selection of solvent recovery equipment which are generally observed. If the vapor-air mixture is well above the upper explosive limit, it is also likely to be above its solvent dew-point at that pressure, and it is usually easiest merely to cool the mixture down to the solvent dew-point where the vapor will start to condense out on the cooling surface. The condensation will continue as the temperature is reduced until the lowest temperature available is reached. This is commonly the temperature of the natural surface water at that particular season of year. Artificial refrigeration may be used to reduce the temperature of the gas still further if the economics of the process permit. But even with artificial refrigeration, considerable amounts of uncondensed vapor remain in the air (or substitute) used in the process, and cannot economically be discarded. It is therefore advisable to use the gas over again in order to avoid throwing its vapor content away. This is done by recycling the gas back to the point where the solvent is being vaporized, instead of using fresh gas. This means a closed process, everything made tight with respect to the surroundings. It must be remembered that when air is used as the carrier gas, the condensation of the mixture by cooling may reduce that percentage of the vapor below the upper explosive limit, with resulting danger of explosion in the apparatus.

In some industries, as in the recovery of natural gasoline from natural gas, where the concentration of condensable solvent is well below its dew-point at ordinary pressures, it is very common to compress the mixture to a high pressure for the purpose of pumping the gas through long pipe lines. This also raises the partial pressure of the solvent in the gas in the same proportion, so that its vapor pressure becomes higher than that which it has at ordinary pressures, and thus makes possible the removal of a large part of it from the residual gas by cooling in suitable condensers.

In most cases, however, it is not feasible, because of the narrow margin of safety, to attempt to maintain the solvent concentration in the air at a sufficiently high percentage to permit solvent recovery by simple cooling and concentration. Under such circumstances, the usual practice is to keep the mixture dilute enough so that the solvent vapor content never rises above the lower explosive limit. This of course makes the solvent much harder to condense and at ordinary pressures usually precludes the use of simple condensation. It is therefore necessary to make use of some device which will cause the vapor pressure of the condensed solvent to be appreciably lower than it would normally be at the same temperature.

There are two well-known methods for doing this. One method consists in dissolving the condensed solvent in some liquid in which it is readily soluble. This has the effect of lowering its pressure in proportion to the amount of dissolving liquid used, so that if a large enough amount of the liquid is used, the effective partial pressure of the dissolved solvent may be reduced to a very low figure, and the residual vapor left behind in the air will be reduced to a correspondingly low percentage. This method is usually called absorption by scrubbing or washing, and is frequently carried out by means of a scrubbing tower up through which the solvent-laden air is blown and down through which the scrubbing liquid is allowed to flow. Thus the descending liquid washes the soluble solvent from the ascending gases. The resulting liquid draining from the bottom of the tower must then be treated by some further process—usually fractional distillation—in order to separate the two materials for reuse.

Quite often the solvent content of the carrying gas is so low that it would take an inordinate amount of scrubbing liquid to reduce the partial pressure to such a point that the solvent would be dissolved to any appreciable extent by the liquid. Under such circumstances,

the most suitable method for separating the solvent from the gas is by what is known as adsorption on a solid adsorbing agent such as activated carbon. These solid adsorbing agents have the peculiar property of holding the adsorbed vapor so tightly on their surfaces that the resulting pressure of the solvent tending to escape from the surface is extremely small, in some cases almost unmeasurable. All that is necessary is to bring the solvent-laden air into contact for a short time with the solid being used as an adsorbent, and the solvent is quickly picked up. If the solid is free from adsorbed vapor at the start, it possesses tremendous adsorbing power and may easily free the air entirely from vapor. As the adsorbing agent becomes loaded with vapor, however, its adsorbing power naturally diminishes until the point is reached where it must be replaced by fresh solid. The saturated solid is then subjected to a stripping process which consists of bringing it into contact with some hot, readily condensable vapor like steam. This reverses the adsorption process and revaporizes the adsorbed vapor. The vaporized mixture is then taken to a condenser where it completely condenses, and the solvent and the water are afterward separated. This separation is effected by fractional distillation if the two substances in the liquefied state are soluble in each other, or by decantation if they are immiscible. The use of solid adsorbents is generally a batch process so far as the solids are concerned, the batch of solid being used until it becomes saturated and then removed for further treatment, its place being taken by a fresh batch, usually in a separate container which is cut into the system when the previous one is cut out.

In small installations, it does not ordinarily pay to use too complicated a system, but in large ones, it may frequently be worth while to use a combination of two or more of these several methods rather than one alone. There is no natural antagonism between them.

In many instances, the designing engineer is called upon to work out a solvent recovery system for some industrial process which is already in existence and which it is often inadvisable to change appreciably in order to install the recovery equipment. It is much more satisfactory, however, to have the recovery equipment and the preceding part of the process designed at the same time, modifying both to take greatest advantage of the operation of the other. This is particularly true where there is fire risk or where the solvent vapor is poisonous.

This book makes no attempt to consider the process by which the solvent to be recovered reaches the vapor state, as that is bound up in the manufacturing process in which the solvent is used. Nor is the subsequent treatment of the recovered solvent to make it suitable for reuse to be considered here, as this frequently involves complicated treatments such as fractional distillation, for which there is a large and satisfactory literature available. It is presumed that the reader is interested in becoming reasonably familiar with the basic principles on which the several recovery methods are based; therefore the book starts with the fundamental physical chemistry, and then applies that to the discussion of these methods in turn. It makes no attempt to treat the economics of the several processes, as these vary both with time and locality. It is hoped that a sufficient number of examples have been given to permit the reader to follow the text without difficulty.

Chapter 2

Gases and Vapors

The Gas Laws

A substance, under suitable conditions, may exist in the form of a liquid, a solid, or a vapor. When in the vapor state it is subject to the laws governing that state, *i.e.*, the gas laws. These laws have to do with the effect of changes in pressure and temperature upon the condition of the vapor. Increasing the temperature of a vapor tends to increase its volume, lowering the temperature having the reverse effect. If the pressure on a given amount of gas is kept unchanged, it has been found that temperature changes have definite effects upon its volume. For instance, if the gas is at 0°C ., and is cooled 1°C . at constant pressure, the gas will be found to have decreased in volume approximately $1/273$ of its volume at 0°C . If the gas is cooled another degree, its volume would be decreased to $271/273$ of its volume at 0°C . It would appear that if the gas were to be cooled to -273°C ., its volume would become zero. Actual gases and vapors, however, condense and become solid before this temperature, which is known as Absolute Zero (-273.1°C . or -459.69°F .), is reached, the hypothetical gas which follows this law throughout all temperature ranges being known as the Perfect Gas.

The Effect of Temperature on Vapors

The effect of temperature on the volume of a perfect gas at constant pressure can be expressed mathematically by the equation

$$\frac{V_1}{T_1} = \text{constant} = \frac{V_2}{T_2}$$

where V represents the volume of the gas, and T the absolute temperature, that is, the number of degrees above absolute zero.

Example 1. A perfect gas at 1 atmosphere pressure at 15° C. occupies 100 cubic feet. What will be its volume at 100° C.?

$$\frac{V_1}{T_1} = \text{constant} = \frac{V_2}{T_2}$$

$$\frac{100}{(273 + 15)} = \frac{V_2}{(273 + 100)}$$

$$V_2 = 129.5 \text{ cubic feet, at } 100^\circ \text{ C.}$$

Example 2. A gas occupies 100 liters at 60° F.; what will be its volume at 500° F.?

$$\frac{100}{(459.7 + 60)} = \frac{V_2}{(459.7 + 500)}$$

$$V_2 = 184.6 \text{ liters at } 500^\circ \text{ F.}$$

The Effect of Pressure on Vapors

Doubling the pressure at constant temperature on a perfect gas halves its volume. This can be expressed by the equation:

$$(2) \quad PV = \text{constant}$$

Equations (1) and (2) can be combined, giving

$$(3) \quad \frac{PV}{T} = \text{constant (the Perfect Gas Law)}$$

where P represents absolute pressure.

Example 3. A gas occupies 1 cubic foot at 100 pounds per square inch gauge pressure and 400° F. What will be its volume at zero pounds gauge and 200° F.?

(Zero pounds gauge pressure = 14.7 pounds per square inch absolute pressure)

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$(100 + 14.7)(1) = (14.7)(V_2)$$

$$(459.7 + 400) = (459.7 + 200)$$

$$V_2 = 5.98 \text{ cubic feet.}$$

Deviations from Gas Laws

The deviation of actual gases and vapors from the perfect gas laws is greater, the greater the pressure on the gas, and the nearer the gas to its condensation temperature. Complicated equations have been developed to express more exactly the behavior of actual gases with respect to changes in temperature and pressure. These equations are, however, beyond the scope of this book. The deviation of actual gases and vapors from the perfect gas law at ordinary pressures is not excessive, and the simplicity of calculations of vapor volumes usually warrants the use of this law.

Where higher pressures or lower temperatures cause deviations of 5% or more, it is advisable to introduce a correction term into the perfect gas formula, as follows:

$$PV = \mu NRT,$$

where P represents the absolute pressure,

V the volume,

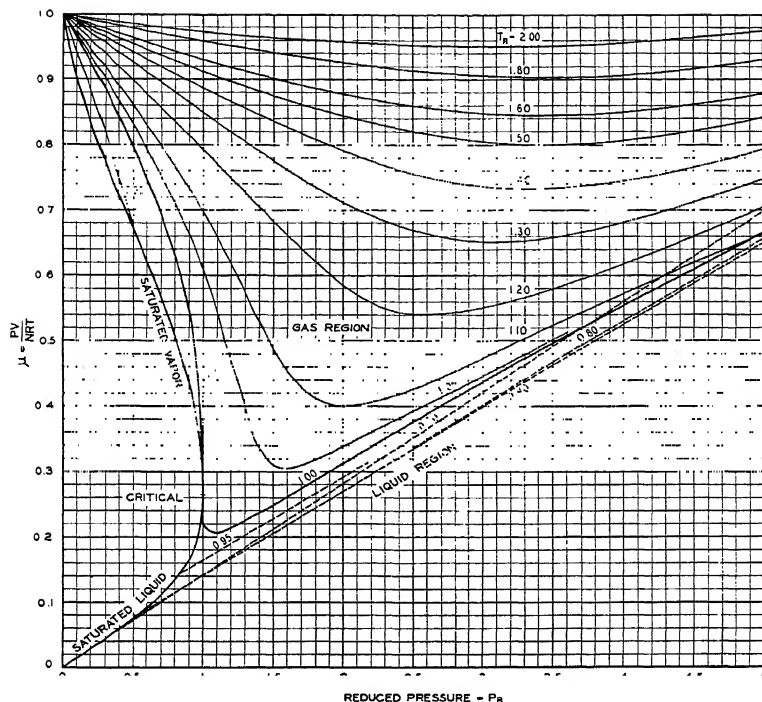
μ a correction factor,

N the number of mols (molecular weights) of the gas,

R the gas constant; [$R=1546.0$ when P is expressed in pounds per square foot absolute pressure, V is in cubic feet, and T is in degrees Rankine ($^{\circ}\text{F. absolute} = ^{\circ}\text{F.} + 459.69$); $R=0.08206$ when P is in atmospheres, V in liters, and T in $^{\circ}\text{Kelvin}$ ($^{\circ}\text{C. absolute} = ^{\circ}\text{C.} + 273.16$];

T the absolute temperature.

The correction factor μ (Greek letter mu) is obtained from the diagram, Figure 1, where μ is plotted against Reduced Pressure (P_R) for several values of Reduced Temperature (T_R). The reduced pressure is the actual pressure divided by the critical pressure of the gas in question, and the reduced temperature is similarly the actual temperature divided by the critical temperature of the gas, all in absolute units.



From Weber "Thermodynamics for Chemical Engineers"
(John Wiley & Sons, Inc.)

FIGURE 1.

Example 4. The critical pressure and temperature of propane (C_3H_8 , molecular weight 44) are 43 atmospheres and $369^\circ K$. respectively. To calculate the volume occupied by one gram of propane gas at $443^\circ K$. and 21.5 atmospheres absolute pressure, proceed as follows:

$P_R = 21.5/43. = 0.5$, $T_R = 443/369. = 1.20$, and from the chart,
 $\mu = 0.897$

$$P \times V = \mu \times N \times R \times T$$

$$21.5 \times V = 0.897 \times \frac{1 \text{ gram}}{44} \times 0.08206 \times 442.5$$

whence $V = .0344$ liter.

The use of the perfect gas formula, for comparison, gives $V = .0384$ liter, an error of about

The following table gives critical values for some of the common gases and vapors.

Substance	Formula	Critical Pressure (atm.)	Critical Temp. (° K.)
Acetone	C_3H_6O	47.	508.
Ammonia	NH_3	111.5	406.
Benzene	C_6H_6	48.	562.
Butane (<i>n</i>)	C_4H_{10}	36.	426.
Butyl alcohol (<i>n</i>)	$C_4H_{10}O$	48.	560.
Carbon disulphide	CS_2	76.	546.
Carbon tetrachloride	CCl_4	45.	556.
Chlorobenzene	C_6H_5Cl	45.	632.
Ethyl acetate	$C_4H_8O_2$	38.	523.
Ethyl alcohol	C_2H_6O	63.	516.
Ethyl ether	$C_4H_{10}O$	35.5	467.
Heptane	C_7H_{16}	27.	540.
Hexane	C_6H_{14}	30.	508.
Isobutyl acetate	$C_6H_{12}O_2$	31.	563.
Isobutyl alcohol	$C_4H_{10}O$	48.	538.
Methyl acetate	$C_3H_6O_2$	46.	507.
Methyl alcohol	CH_4O	79.	513.
Methyl ether	$C_2H_6O_2$	52.	400.
Octane (<i>n</i>)	C_8H_{18}	25.	569.
Pentane (<i>n</i>)	C_5H_{12}	33.	470.
Propane (<i>n</i>)	C_3H_8	43.	369.
Toluene	C_6H_8	42.	591.
Water	H_2O	218.	647.

Mixtures of Vapors. Partial Pressure

When a gas or vapor consists of a mixture of two or more gases or vapors, each individual vapor behaves as if it alone were present in the space occupied in the mixture. Thus if a mixture of equal volumes of oxygen and nitrogen be held at one atmosphere pressure, the actual pressure exerted by the nitrogen (its partial pressure) would be one-half atmosphere, and if the oxygen were to be removed from the mixture by some suitable chemical, the pressure exerted by the remaining nitrogen against the walls of the containing vessel would equal the partial pressure, one-half atmosphere.

There is accordingly a relation between the pressure which a given gas exerts when in a mixture of gases, and the percentage by volume of the gas in the mixture. If $100x$ represents the percentage by volume of the

given gas in the mixture, the partial pressure (p) of the gas can be calculated by the equation:

$$(4) \quad p = \pi x,$$

where π is the total pressure exerted by the mixture.

Example 5. Air consists of a mixture of 21.0% by volume of oxygen, 78.0% by volume of nitrogen, and 1.0% by volume of argon, with negligible amounts of other gases. If air exists at 760 mm. of mercury pressure, calculate the respective partial pressures of the constituents.

$$\text{Oxygen } p = 760 \times .210 = 158.6 \text{ mm.}$$

$$\text{Nitrogen } p = 760 \times .780 = 592.8 \text{ mm.}$$

$$\text{Argon } p = 760 \times .010 = 7.6 \text{ mm.}$$

Avogadro's Law

Another relationship between gases and vapors is that of Avogadro, *i.e.*, that equal volumes of different gases at the same temperature and pressure contain the same number of molecules. This means that in a volume of air containing just 1000 molecules, there would be 210 molecules of oxygen, 780 of nitrogen, and 10 of argon, and that the symbol x in equation (4) represents that fraction of the total molecules consisting of the gas in question. This is known as the molecular or mol fraction.

$100x$ = percentage by volume (for gases only)

Calculation of Percentage by Weight

In order to calculate the percentage by weight of the constituents of a gas if the percentage by volume is known, the molecular weights of the respective constituents must be known.

Example 6. Calculate the percentage by weight of the constituents of air. The molecular weights are: oxygen (O_2) = 32, nitrogen (N_2) = 28, argon (A) = 40.

Basis for calculation, 100 molecular weights of air.

$$\text{Weight of } O_2 = 21.0 \times 32 = 672$$

$$\text{Weight of } N_2 = 78.0 \times 28 = 2184$$

$$\text{Weight of A} = 1.0 \times 40 = 40$$

$$\text{Total weight} = \underline{2896}$$

$$\text{Percentage by weight of O}_2 = \frac{672 \times 100}{2896} = 23.10\%$$

$$\text{Percentage by weight of N}_2 = \frac{2189 \times 100}{2896} = 75.52\%$$

$$\text{Percentage by weight of A} = \frac{40 \times 100}{2896} = 1.38\%$$

$$\text{Total} = 100\%$$

Calculation of Percentage by Volume

The reverse calculation, that of volume percentage from weight percentage, is made as follows:

Example 7. Dry flue gas at an absolute pressure of 15 pounds per square inch has the following analysis by weight.

CO₂ (Carbon dioxide) = 14.7%, O₂ = 8.6%, N₂ = 76.7%.

Calculate the analysis in percentage by volume. The molecular weight of CO₂ = 44.

Basis for calculation, 100 parts by weight of flue gas.

$$\text{Mols of CO}_2 = \frac{14.7}{44} = .334$$

$$\text{Mols of O}_2 = \frac{8.6}{32} = .269$$

$$\text{Mols of N}_2 = \frac{76.7}{28} = 2.74$$

$$\text{Total mols} = \overline{3.343}$$

$$\text{Percentage by volume of CO}_2 = \frac{.334 \times 100}{3.343} = 10.0\%$$

$$\text{Percentage by volume of O}_2 = \frac{.269 \times 100}{3.343} = 8.0\%$$

$$\text{Percentage by volume of N}_2 = \frac{2.74 \times 100}{3.343} = 82.0\%$$

$$\text{Total} = \overline{100.0\%}$$

Chapter 3

Vaporization

Vapor Pressure

All substances, either liquid or solid, theoretically vaporize to some extent, the degree depending upon conditions of temperature and external pressure. At any given temperature a substance has a definite tendency to pass into the vapor state, and this tendency, when measured in terms of pressure, is called its vapor pressure. If a pure, volatile, substance be confined in a given space at a fixed temperature, it will vaporize until the pressure of the substance in the space above the liquid (or solid) is equal to its vapor pressure at that temperature, and no further vaporization will occur unless some of the vapor is removed, thus lowering its pressure.

Within limits of ordinary pressures the pressure of a vapor above its liquid, and in equilibrium with the liquid, is independent of the presence of other gases and vapors. When other gases are present, its pressure is spoken of as its partial pressure.

Clapeyron Equation

There is no simple rule for expressing the relation between the temperature and the vapor pressure of a substance. A modified form of the Clapeyron equation gives an approximate relation which is of considerable value.

$$(5) \quad \frac{d \log_e P}{dT} = \frac{L}{RT^2}$$

where $\log_e P$ is the natural or Napierian logarithm ($2.303 \times \log_{10}$) of the pressure P , T is the absolute tem-

perature, L is the latent heat of vaporization of one mol of the substance, and R is the gas constant (1.99 when L is expressed in heat units per unit molecular weight). This equation can be used over short temperature ranges, on the assumption that L is a constant (L changes slightly with the temperature), in its integrated form:

$$\log_e \frac{P_2}{P_1} = \frac{L}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Example 8. The vapor pressure of water at 100° C. is 14.7 pounds per square inch; calculate the vapor pressure at 150° C. The latent heat of vaporization of water at 100° C. is 970.4 calories per gram mol.

$$\log_e \frac{P_2}{14.7} = \frac{970.4}{1.99} \left(\frac{1}{100 + 273} - \frac{1}{150 + 273} \right)$$

$$\log_e \frac{P_2}{14.7} = 1.535$$

$$\frac{P_2}{14.7} = 4.65$$

$$P_2 = 68.5 \text{ pounds per square inch.}$$

The actual vapor pressure of water at 150° C. is 69.3 pounds per square inch. This indicates the degree of accuracy of this equation for such temperature changes. A better approximation would have been obtained by taking L at the average temperature, i.e., 125° C.

Trouton's Rule

Frequently, occasion arises for an approximate vapor pressure curve for a substance whose latent heat of vaporization is not known. Such an approximation can be obtained if the boiling point of the liquid at atmospheric pressure be known, by the use of Trouton's Rule:

$$(7) \quad \frac{L}{T} = 20.5$$

where L is expressed in gram calories per gram mol, and T is the boiling temperature in degrees centigrade abso-

lute ($^{\circ}\text{K}$). This rule does not hold for water, acids, or alcohols, but for most other organic liquids it is fairly close to the fact.

Example 9. Benzene, C_6H_6 , boils at 80.2°C . at 760 mm. pressure. What is its boiling temperature at 300 mm. pressure?

$$\frac{L}{(80.2 + 273)} = 20.5 \quad L = 7250.$$

$$\log_e \frac{760}{300} = \frac{7250}{1.99} \left(\frac{1}{T_2} - \frac{1}{273 + 80.2} \right)$$

$$T_2 = 324.^{\circ}\text{K}. = 51.^{\circ}\text{C}.$$

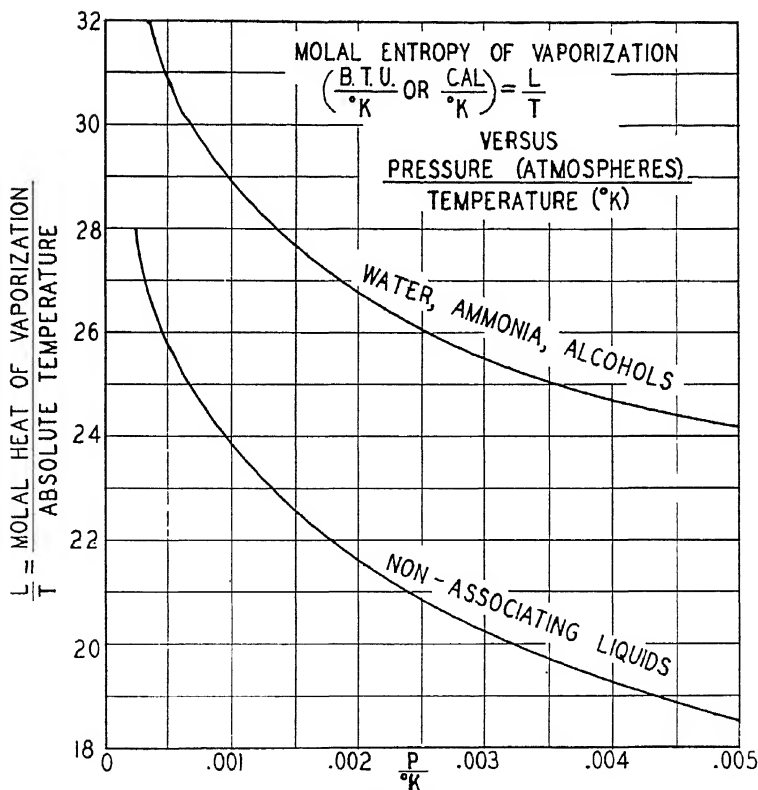


FIGURE 2.

The temperature at which the vapor pressure of benzene is actually 300 mm. is 52.8° C.

Hildebrandt Curves

Values for $\frac{L}{T}$ can be read from Figure 2, using the lower curve for most organic liquids, and the upper curve for water, ammonia, and alcohols. The abscissae

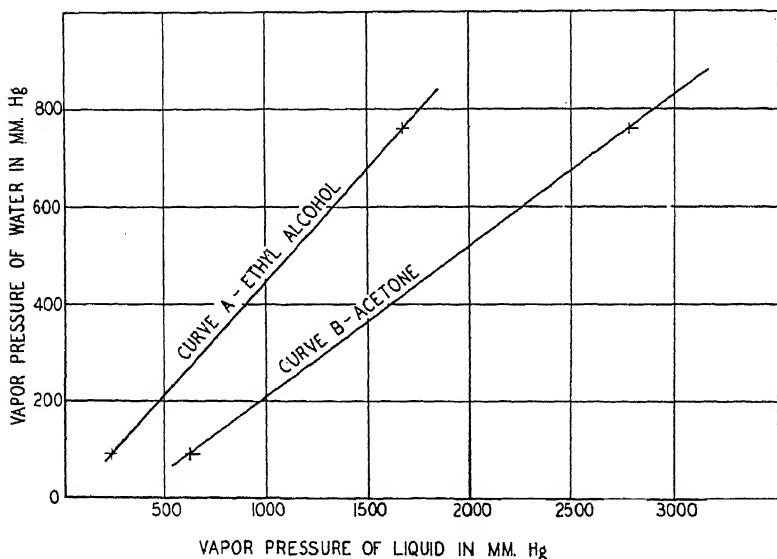


FIGURE 3.

are the ratios of the vapor pressure in atmospheres to the temperature in °K (°C. absolute). Thus for benzene boiling at 80.2° C. at 760 mm. (1 atmosphere),

$$T \quad \frac{1}{(80.2 + 273)} = .00283, \text{ and } \frac{L}{m} = 20.45$$

Dühring's Rule

When two points on a vapor pressure curve are known, there is another approximate method for calcu-

lating the vapor pressure. This consists of plotting the vapor pressures of water as ordinates and the vapor pressures of the liquid in question at the same temperatures as abscissae. Thus at 50°C. , the vapor pressure of water is 91.98 mm. while that of ethyl alcohol at the same temperature is 219.8 mm. These two pressures would give one point on curve *A* shown on Figure 3.

A series of points is found to lie on what is practically a straight line, curve *A*. Therefore if two points for any liquid be known, a straight line drawn through them, curve *B*, will give a vapor pressure curve which is remarkably near the true one.

Chapter 4

Liquid Mixtures

Raoult's Law

The vapor pressure of a volatile liquid is lowered by the introduction of soluble substances into it, the lowering being approximately proportional to the amount of foreign substance dissolved. The effect is expressed by Raoult's law:

$$(8) \quad p = p_0 x$$

where p is the vapor pressure of the liquid after the addition of the foreign substance; p_0 is the vapor pressure of the pure liquid at the same temperature, and x is the mol fraction of the pure liquid in the mixture.

Example 10. Water has a vapor pressure of 760 mm. at 100° C. What will be the vapor pressure of a 10% sugar solution at that temperature? The molecular weight of water is 18 and that of sugar is 342.

Basis = 100 parts of solution by weight

$$\begin{aligned} \frac{10}{342} &= .0292 \text{ mol sugar} \\ \frac{90}{18} &= 5.00 \text{ mols water} \\ &\hline &5.0292 \text{ total mols} \\ \text{mol fraction of water} &= \frac{5.00}{5.0292} \\ p &= \frac{5.00}{5.0292} \times 760 = 755.8 \text{ mm.} \end{aligned}$$

The vapor pressure of the water at 100° C. has therefore been lowered 4.2 mm. by the dissolved sugar.

Salts, acids, and other substances which dissociate in aqueous solution give a greater lowering of vapor

pressure than is calculated from their molecular weight. Solutions of substances in organic solvents are usually not dissociated, but are sometimes "associated," giving effective lowerings of vapor pressure less than those calculated. Raoult's Law can be safely used for most liquids from values of x from 1.00 down to 0.95. Below 0.95 it is not safe except in special cases, and recourse should be had to experimental data.

Henry's Law

A volatile substance dissolved in a solvent exerts a partial pressure proportional to the amount of the substance present. This can be expressed by the equation:

$$(8a) \quad p = ax$$

where p is the partial pressure (of the volatile substance) over the solution; x is the mol fraction of the volatile material, and a is a constant. Raoult's Law is therefore a special case of Henry's Law where $a = p_0$. Henry's law is to be used for dilute solutions, where x is less than 0.05.

Example 11. The partial pressure of ammonia over an aqueous solution containing 1.95% NH_4OH is 7.6 mm. Calculate the partial pressure of a solution containing 1.0% NH_4OH .

For very dilute solutions, mol percentage ratios are practically equivalent to weight percentage ratio; therefore, by a ratio,

$$\begin{array}{rcl} p_2 & 1.0 \\ 7.6 & 1.95 \\ p_2 & = 3.9 \text{ mm.} \end{array}$$

For very dilute solutions, where there is a chemical combination between solute and solvent, Henry's Law does not hold exactly. This is true for a solution of ammonia in water; therefore the above calculation is only approximate. For more accurate calculations, the relation between the constant of Henry's Law and the concentration, pressure, and temperature should be determined experimentally.

Mixtures of Two Volatile Liquids

Two volatile liquids, when mixed, lower each other's vapor pressures. This is shown in Figure 4 at some fixed temperature t , for two liquids, A and B , the latter being the more volatile. In this diagram, vapor pressures are shown as ordinates and mol fractions of B (x_B) as abscissae. The left-hand side represents pure A and the right-hand side pure B . If mixtures of A and B followed Raoult's Law in all proportions, which is less

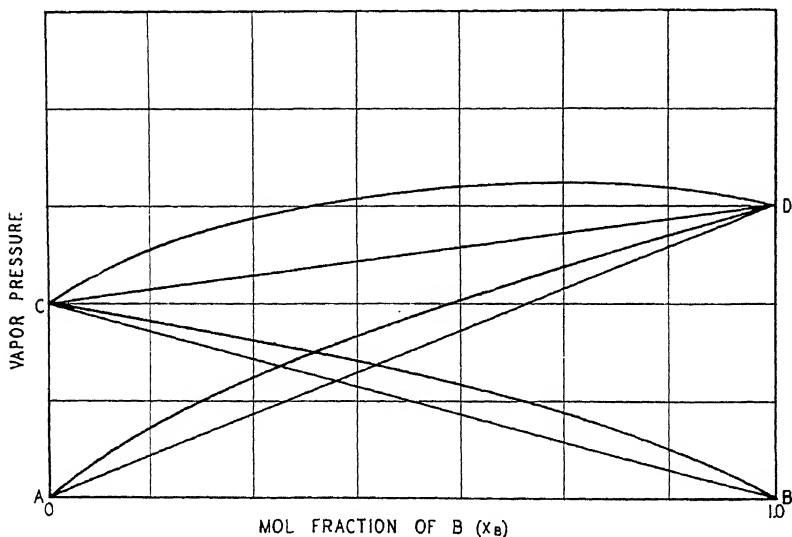


FIGURE 4.

usual, the partial pressure of B would be represented by the straight line AD , while that of A would be represented by the straight line CB . The sum of the two pressures or the total pressure would therefore be shown by the straight line CD . If the mixture does not follow Raoult's Law, the lines will not be straight, their shape being obtained by experiment. The curved lines connecting the points A , B , C , and D show a common type of curve for such mixtures.

Partially Miscible Liquids

If the two volatile liquids do not mix completely, an important modification of the vapor-pressure diagram is obtained. The diagram in Figure 5 shows such a mixture of two liquids *A* and *B*, *A* being soluble in *B* to the extent indicated by the point *C*, and *B* being soluble in *A* to the extent indicated by the point *D*.

If equal parts of *A* and *B* are mixed, two layers will be formed, one of which will have the composition *D*,

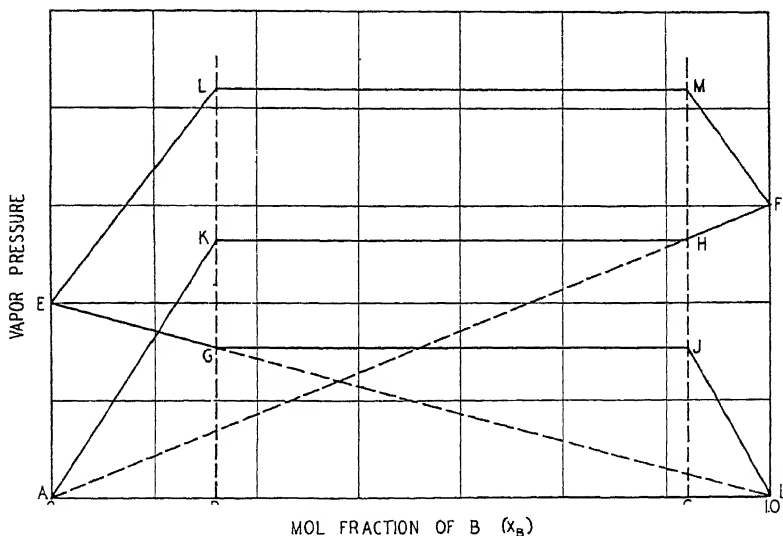


FIGURE 5.

and the other the composition *C*. The vapor pressure of pure *A* is represented by the point *E*, and that of pure *B* by the point *F*. The partial pressure of *A*, if the mixture follows Raoult's Law within the limits of solubility, will follow along the straight line *EB*, the line stopping at the limit of solubility of *B* in *A*, the remaining dotted line merely indicating the direction. Similarly, the partial pressure of *B* will follow the line *FA*, stopping at *H*. For mixtures between the com-

positions D and C , where two layers are present, the partial pressure of A will remain constant at the value H , as indicated by the horizontal line HK , while that of B will remain as shown by the line GJ . For mixtures outside these limits, if they follow Henry's Law, the partial pressure of B will be represented by the straight line KA , and in the case of A by the straight line JB . The total pressure of such a mixture will be represented by the lines EL , LM , and MF , the total pressure being greater than that of either of the pure substances alone. In case the mixtures fail to follow Raoult's and Henry's Laws within the limits indicated, the lines EG , AK , HF , JB , EL , and MF will not be straight, but the lines GJ , KH , and LM will always be straight and horizontal.

Completely Immiscible Liquids

Where the liquids mixed are almost completely insoluble in each other, they will form separate layers; the partial pressure of each will be that of the pure liquid and the total pressure the sum of the two.

Chapter 5

Distillation of Liquid Mixtures

The composition of the vapor evolved from a mixture of two or more volatile liquids has a definite relation to the composition of the liquid from which it comes. For liquid mixtures which follow Raoult's Law, this composition can be calculated, but for others it is necessary to obtain experimental data.

Binary Mixtures

For binary mixtures of liquids soluble in each other in all proportions, the relation between the composition of the vapor and of the liquid can be shown by means of a diagram such as Figure 6.

In this diagram the abscissae, x , represent composition of the liquid mixture in % A , while the ordinates, y , represent the composition of the vapor evolved by the liquid, also expressed in % A . Suppose that the curve ABC represents the relation between the composition of the liquid and the vapor for a certain mixture. Then a liquid with 30% of the one component will produce a vapor containing 40% of that component. Or if the curve $ADEFC$ represented the relation, the vapor in equilibrium with a 30% solution would contain 60% of that component.

Types of Liquid Mixtures

There are in general three types of liquid mixtures soluble in all proportions. The first type, represented by the curve ABC , produces a vapor which is always richer in the more volatile component than the liquid. The second type, represented by the curve $ADEFC$,

produces a vapor which is richer than the liquid in the more volatile component up to the composition represented by the point *E*. For greater concentrations (between *E* and *C*) the vapor is poorer in that component, and at the point *E*, the vapor has the same

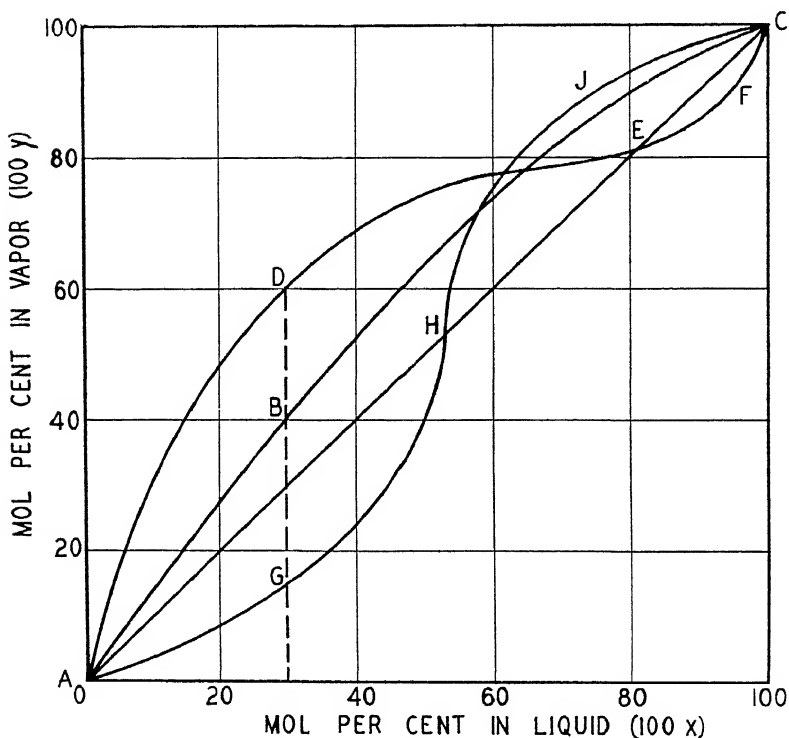


FIGURE 6.

composition as the liquid from which it comes. Such a mixture of liquids forms a mixture, at the composition *E*, of constant boiling point. The liquid composition remains unchanged when a mixture of constant boiling point is being distilled, and the total vapor pressure curve passes through a maximum at that composition.

On the other hand, a mixture illustrated by the curve $AGHJC$ has a point of minimum vapor pressure at the composition H , and such a mixture is known as one of maximum boiling point. The boiling point curves of these mixtures at constant pressure are shown in Figure 7, which has temperature as ordinates and composition of the liquid (x) as abscissae.

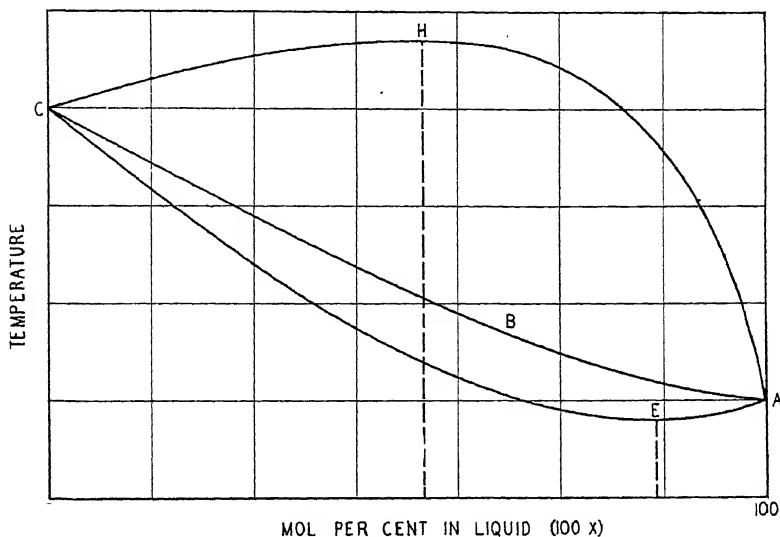


FIGURE 7.

In this diagram, the curve ABC is the boiling point curve of mixtures similar to that giving the curve ABC in Figure 6. The curve AEC corresponds to $ADEFC$ in Figure 6, the point E being the minimum boiling mixture. The curve AHC corresponds to $AGHJC$ in Figure 6, the point H being the maximum boiling point.

Liquids which are not miscible in all proportions, within the range in which two layers are present, act in a similar manner to constant boiling mixtures, the composition of the vapor and the boiling temperature at constant pressure remaining unchanged, so long as

the two layers are present. When one of the layers has disappeared, the remaining layer behaves like one of the preceding types of miscible liquids.

The relation between the liquid and vapor can also be shown on the temperature composition diagram (Figure 8).

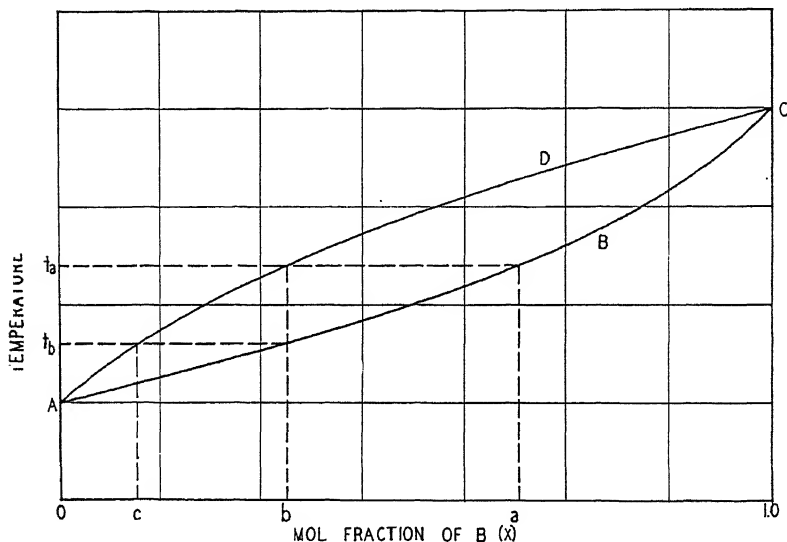


FIGURE 8.

In this diagram, the curve ABC is the boiling point curve at constant pressure for a binary mixture which forms no constant boiling mixtures, and the curve ADC represents the vapor in equilibrium with it. Thus a mixture of the composition a boils at the given pressure at the temperature t_a , giving a vapor whose composition is b . The vapor of the composition b can be condensed and would boil at the temperature t_b , giving a vapor of the composition c . If this process be repeated, a vapor consisting of pure A would finally be obtained. This continued reboiling of condensed

vapors is the basis for the separation of volatile liquids by fractional distillation.

Mixtures of liquids which form constant boiling mixtures either of the minimum or maximum variety cannot be separated completely into their pure components by fractional distillation at constant pressure alone; one product of complete fractionation is always the constant boiling mixture, and the other, one of the pure components.

Chapter 6

Condensation of Mixed Vapors

The condensation of mixed vapors can be readily followed by means of the t - x diagram. Figure 9 is such a constant pressure diagram for a binary mixture, miscible in all proportions, and completely separable by fractional distillation.

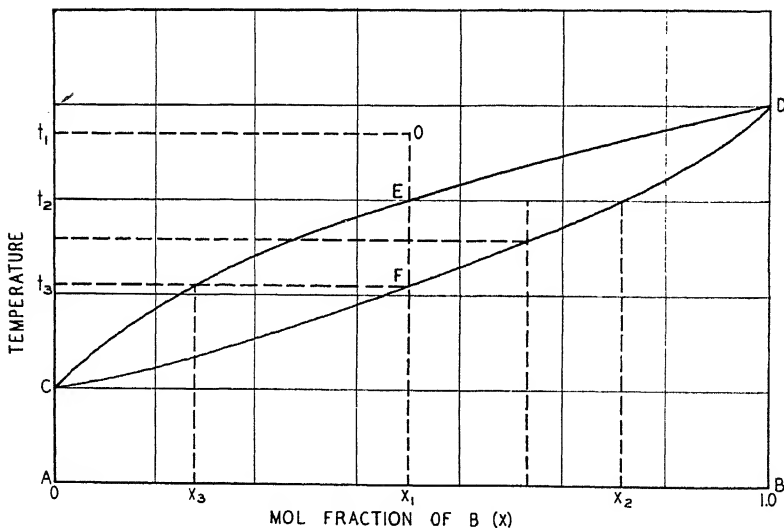


FIGURE 9.

The pure liquid A boils at the temperature C , while B boils at the temperature D . The boiling point curve of the mixture is represented by the curve CFD , and the vapor in equilibrium with the liquid is shown by the curve CED , as explained in the preceding chapter.

Suppose that a vapor mixture of the composition x_1

is at the temperature t_1 . It will be superheated vapor at this temperature, and if the temperature is gradually lowered, no change in the vapor other than a decrease in volume will occur until all of the superheat has been lost, which will occur when the temperature has reached t_2 . At this point condensation will commence, the liquid which first appears having the composition x_2 . The remaining vapor will therefore become richer in the component A , as cooling continues, while the liquid, though still richer in B than the original composition x_1 , will gradually grow poorer with respect to that component. If all the liquid condensed is kept in contact and in equilibrium with the remaining vapor, when the temperature has dropped to t_3 , all the vapor will have condensed, and the condensate will have the original composition of the vapor x_1 . The last of the vapor to condense under these conditions will have the composition x_3 .

Differential Condensation

If the liquid in such a condensation process is removed from contact with the vapor as fast as it forms, the final concentration of the vapor will not be limited by the value x_3 , but the vapor will grow progressively richer in A , until the final vapor to condense will consist of pure A . It is therefore possible to obtain separation of vapor mixtures by means of condensation as well as by distillation, and both processes are combined in fractional distillation.

Mixtures of Vapors and Gases

A gaseous mixture may consist of several substances which condense easily at ordinary temperatures together with some that are condensable only at much lower temperatures, such as the so-called permanent gases, air, carbon dioxide, and others. Under these conditions, the condensable vapors condense practically

alone, the liquid containing only such amounts of the non-condensable gases as may be soluble in them at the condensation temperature and pressure. The amount of vapor remaining in the gas can be calculated from the vapor-pressure curves of the condensed vapor, and the amount condensed can be obtained by difference.

Example 12. Air at 120° F. and normal barometer, 29.92 inches of mercury (Hg), is passed over benzene (C_6H_6) until it is saturated at that temperature. The mixture of air and vapor is then removed to a condenser where it is cooled at constant pressure to 100° F. Calculate the pounds of benzene condensed per pound of air. The vapor pressure of benzene at 120° F. is 10.2" Hg, and at 100° is 6.5" Hg. The molecular weight of benzene is 78, and that of air is approximately 29.

Total pressure = 29.92" Hg (normal barometer)

Since the air is saturated at 120° with benzene, the partial pressure of benzene in the air will equal the vapor pressure of benzene at that temperature. Similarly, the partial pressure at 100° will equal the vapor pressure at 100°.

$$\begin{array}{ll}
 \text{At 120° partial pressure of benzene} & = 10.2'' \\
 \text{partial pressure of air} & = 29.92 - 10.2 = 19.7 \\
 \text{mols of benzene per mol of air} & = \frac{10.2}{19.7} = .518 \text{ mol} \\
 \text{At 100° partial pressure of benzene} & = 6.5'' \\
 \text{partial pressure of air} & = 29.92 - 6.5 = 23.3'' \\
 \text{mols of benzene per mol of air} & = \frac{6.5}{23.3} = .279 \text{ mol} \\
 \text{mols of benzene condensed per mol of} & \\
 \text{air} & = .518 - .279 = .239 \text{ mol} \\
 \text{pounds of benzene condensed per pound} & \\
 \text{of air} & = \frac{.239 \times 78}{29} = .64 \text{ lb.}
 \end{array}$$

Example 13. A mixture of air and ethyl alcohol vapor at 120° F. is cooled to 80° F., during which 50 pounds of alcohol are condensed per 1000 cubic feet of the original mixture. Calculate the percentage by volume of the alcohol in the original mixture. Barometer normal. Molecular weight of ethyl alcohol is 46. Vapor pressure of alcohol at 120° F. is 8.1" Hg, and at 80° is 2.5" Hg.

1 molecular weight of a gas in pounds (1 pound mol) occupies 359 cubic feet at standard conditions (32° F. and 14.7 lbs. per square inch absolute pressure).

1000 cubic feet of the original mixture would contain

$$\frac{1000 \times (459.7 + 32)}{359 \times (459.7 + 120)} = 2.365 \text{ mols of air -}$$

of which there are A mols of alcohol and $(2.365 - A)$ mols of air.

The air at 80° F. would contain $(2.365 - A) \times \frac{2.5}{(29.92 - 2.5)}$ mol of alcohol.

The alcohol condensed per 1000 cubic feet is 50 pounds or

$$\frac{50}{46} = 1.09 \text{ lb. mols.}$$

Therefore:

$$1.09 + (2.365 - A) \times \frac{2.5}{(29.92 - 2.5)} = A$$

$A = 1.195$ mols of alcohol in original mixture.

$$\text{Percentage by volume of alcohol} = \frac{1.195 \times 100}{2.365} = 50.5\%.$$

Chapter 7

Rate and Capacity

All engineering processes require time for their completion, and in many cases the speed or rate at which the process progresses can be estimated by the use of the previously mentioned laws and other relations. A knowledge of the rate is necessary to determine the capacity of the apparatus. This rate is generally called Rate of Reaction.

The rate at which a process or reaction progresses is proportional to the driving force which is causing the reaction to proceed. This driving force is known as the potential of the process, and the greater the potential, the greater the speed. Thus the rate of flow of heat from one body to another is proportional to the temperature difference between the two bodies. The rate of dissolving of a salt is proportional to the concentration difference between the solution and a saturated solution. In solvent recovery work, the rates at which the reactions progress are often proportional to similar potential differences.

Rate of Flow of Heat

One of the commonest and simplest of such reactions is the rate of flow of heat. The introduction of heat into the volatilizing solvent, and its removal from the condensing solvent, are physical reactions which occur in all solvent recovery processes. The usual form of the equation for heat flow by conduction is the following:

$$(9) \quad \frac{dQ}{d\theta} = UA(\Delta t)$$

where dQ is the amount of heat flowing during the time $d\theta$, A is the area of the heating surface through which the heat passes, Δt is the temperature difference between the hot and the cold bodies, and U is a proportionality constant, usually called the coefficient of heat transfer.

Where the flow of heat is by radiation instead of conduction, equation (9) does not hold, as the rate of flow is proportional to the fourth power of the absolute temperature, as shown in the following equation, for the flow from one body to another:

$$(10) \quad \frac{dQ}{d\theta} = cAT^4$$

where T is the absolute temperature and c is the radiation coefficient of the substance.

Rate of Evaporation

The rate of evaporation of a volatile substance from a surface into a gas is proportional to the difference between the vapor pressure of the substance on the surface, and its partial pressure in the surrounding gas. This is expressed by the equation:

$$\frac{dW}{d\theta} = kA(P - p)$$

where dW is the weight of substance vaporized in the time $d\theta$, A is the area of the vaporizing surface, P the vapor pressure of the substance, p its partial pressure in the surrounding gas, and k is a proportionality constant.

In solvent recovery, evaporation of solvent from a solid involves diffusion of solvent from the interior to the surface, as that on the surface evaporates. This diffusion rate can be expressed by a similar equation:

$$\frac{dW}{d\theta} = kA \frac{C - c}{l}$$

where C and c are the solvent concentrations of the

interior and the surface respectively, and l is the distance from the interior to the surface.

Rate of Condensation

In condensation of solvent vapor by cooling or by solution, equation (11) is applicable, in this case P being the partial pressure of the vapor and p the vapor pressure of the condensed or dissolved solvent in contact with it.

All of these equations are what are known as differential equations, that is, they represent conditions at any instant, even though conditions may be continuously changing. In order to use them, they must be modified by a process called integration, to permit them to be used over considerable periods of time. One way of doing this is to make use of average values of the potential or other variable. For example, the rate of heat flow equation, (9), may be written as follows:

$$(13) \quad \frac{Q}{\theta} = UA(\Delta t)_{\text{average}}$$

and this will be a correct relationship if the proper average value is used.

Example 14. In a solvent recovery process, alcohol vapor is being condensed in a surface condenser at 178° F.; the cooling water rises in temperature from 50° F. to 100° F. The coefficient of heat transfer between the alcohol and the cooling water (U) has been found by tests on similar condensers to be 50 British thermal units (B.t.u.) per square foot of condenser surface per degree Fahrenheit temperature difference between the alcohol and the water per hour. It requires 372 B.t.u. to vaporize or condense one pound of alcohol at atmospheric pressure.

The arithmetic average temperature difference between the alcohol and the water is

$$\frac{(178 - 50) + (178 - 100)}{2} = 103^{\circ}$$

Therefore

$$\frac{Q}{\theta} = 50 \times A \times 103 = 5150A$$

If the condenser has 100 square feet of condenser surface,

$$\frac{Q}{\theta} = 5150 \times 100 = 515,000 \text{ B.t.u./hour,}$$

and the amount of alcohol vapor condensed per hour will be $\frac{515,000}{72} = 1385.0$ pounds.

Most differential rate equations may be used in this manner where high precision is not needed.

Capacity of apparatus varies directly as the rate of reaction of the process involved. Thus, in the example just cited, it may be required to find the effect of changing the cooling water temperature on the capacity of the condenser. Suppose that the cooling water entered at 75° F. and rose to 125° F. How much alcohol would the condenser now condense?

$$(\Delta t)_{\text{average}} = \frac{(178 - 75) + (178 - 125)}{2} = 78^{\circ}$$

$$\frac{Q}{\theta} = 50 \times 100 \times 78 = 390,000.$$

Pounds of alcohol condensed per hour $\frac{390,000}{372} = 1050.0$, or
a reduction in capacity of $\frac{1385 - 1050}{1385} \times 100 = 24\%$.

In general, it may be stated that it is necessary to have a rate relationship in order to estimate the capacity or size of any kind of apparatus, and the rate equations based on potential or driving force are likely to prove the most reliable. However, in some cases this type of equation is very complicated and hard to solve, and recourse is often had in such cases to empirical formulas for capacity. These, however, are suitable for interpolation only.

The use of these and similar equations is discussed further under appropriate headings later in this book.

Chapter 8

Adsorption

Solution in Liquids

A gas or vapor, when brought into contact with a liquid in which it is soluble, passes into solution until the partial pressure of the dissolved vapor becomes equal to the partial pressure of the vapor in the surrounding gas, when further solution will cease, equilibrium having been established. Under these conditions, the dissolved vapor will be uniformly distributed throughout the dissolving liquid, and the amount of vapor dissolved per unit volume of liquid will not be affected by the surface exposed to contact between the vapor and the liquid, the surface affecting only the rate of solution. It is true that at the liquid surface, the concentration of the dissolved vapor is greater than at other points in the liquid, but since in most cases the ratio of surface to volume of a liquid is not great, this surface effect does not appreciably affect the total amount of vapor dissolved.

Adsorption on Solids

R. E. Wilson states that, when gas or vapor is brought into contact with a solid substance, there is the same tendency for the vapor to pass into solution in the solid, the vapor collecting on the surface of the solid.¹ But since the solubility of gases and vapors in most solids is exceedingly small, that amount actually dissolved in the interior of the solid can usually be neglected. However, many solid materials, such as carbon which has been activated by treatment with superheated steam at a high temperature, silica gel, activated

¹ *Physical Review, U. S.*, 16, 8 (1920).

alumina, ferric hydroxide gel, and a number of others, possess the power to absorb or "adsorb" gases and vapors on their surfaces to an unusual degree. The mechanism by which this surface adsorption takes place is not actually known, as the effects are beyond the limits of the most powerful microscope, but a careful study by numerous investigators, some of whom are mentioned later, indicates at present that the adsorption is probably caused by a combination of

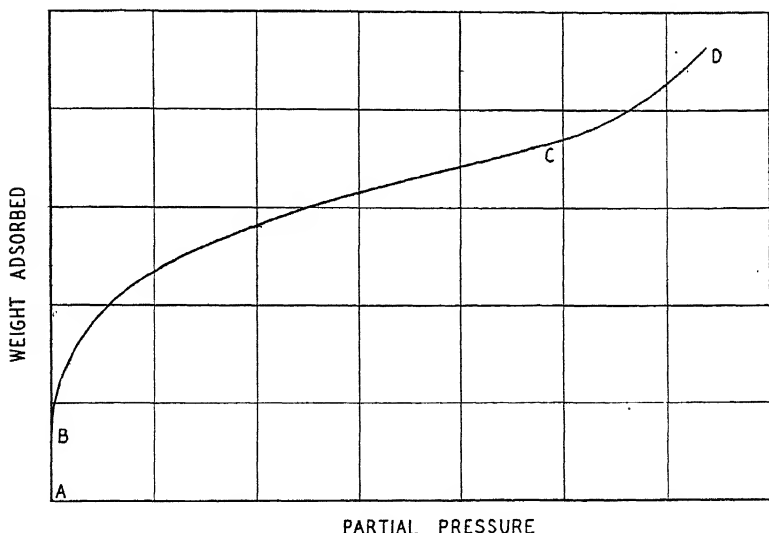


FIGURE 10.

three separate effects. The first of these is the formation on the surface of the solid of a layer of the adsorbed vapor, one molecule deep. The second effect consists of the formation of a second layer of variable thickness held by the attraction between the solid and the vapor, the thickness depending on the strength of the attraction. The third effect is that of the collection on the surface in sub-microscopic capillary openings of a more or less condensed layer of vapor. The three

effects are cumulative, and adsorbing agents possess them in varying proportions to a greater or less degree. They may be shown in Figure 10 taken from the article cited above.

This diagram shows the weight of adsorbed vapor per unit weight of adsorbing solid as a function of the

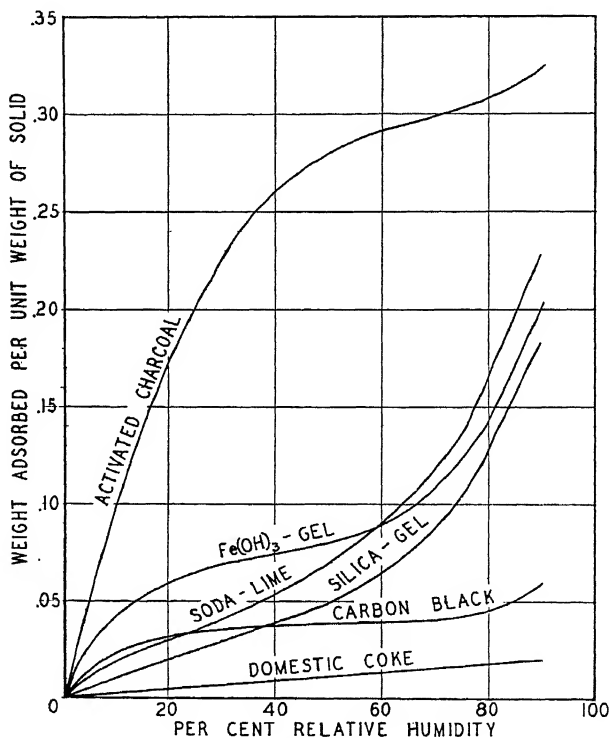


FIGURE 11.

partial pressure of the vapor in equilibrium with the solid. The solid will adsorb vapor from *A* to *B* when the partial pressure of the vapor in the gas is practically zero. When the point *B* is reached, an increase in pressure is needed to increase the adsorption, as indicated by the portion of the curve from *B* to *C*,

which is the range of further adsorption due to molecular attraction; and the last range, from *C* to *D* and further, is that due to capillary condensation.

Common Adsorbing Agents

Figures 11 and 12 show how a number of adsorbing agents adsorb water when exposed to air of varying humidity at a constant temperature of 25° C.² Fig-

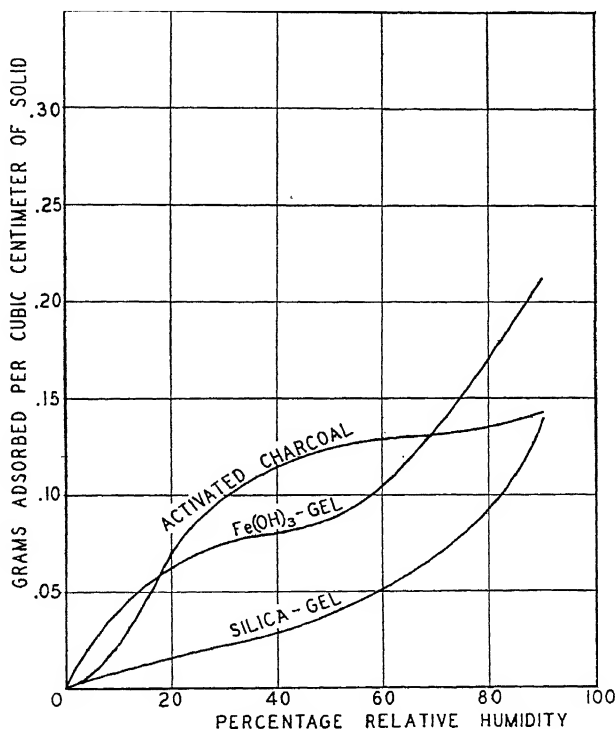


FIGURE 12.

ure 1 shows the weight of water vapor adsorbed per unit of solid as a function of relative humidity for the following substances:

² Data from Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

Activated charcoal
Ferric hydroxide gel ($\text{Fe}(\text{OH})_3 \cdot n \text{H}_2\text{O}$)
Silica gel ($\text{Si}_2 \cdot n \text{H}_2\text{O}$)
Soda-lime ($\text{NaOH} + \text{CaO}$)
Carbon black
Domestic coke

The same data are plotted in Figure 12 for the first three solids, in terms of weight (grams) adsorbed per unit gross volume (cubic centimeter) of solid. These curves indicate how the solids vary in their adsorbing powers. It should be stated also that the adsorptive power of any one substance will depend on the method of its preparation, and also on the character of the vapor adsorbed.

The curves shown above illustrate the type of adsorption effect peculiar to the several substances. Thus, charcoal depends largely on adsorption due to molecular attraction, while silica gel appears to derive its adsorptive power chiefly from the phenomenon of capillary condensation. Ferric hydroxide gel is apparently intermediate in effect.

Although the value of an adsorbing agent depends chiefly on the surface exposed per unit weight of solid, visible porosity is not a sign of a satisfactory material. Thus pumice, though of extreme porosity, is of little value for this purpose.

Many attempts have been made to devise formulas to express the relationship between the amount of vapor or gas adsorbed per unit amount of solid as a function of the partial pressure of the vapor or gas in question. These all apply to equilibrium conditions, when the gas and solid have been left in contact with each other for an infinite length of time.

Freundlich's Adsorption Equation

The formula

$$(14) \quad \frac{x}{m} = ap^{1/n}$$

usually called the Freundlich Equation, is perhaps the

simplest of the formulas that apply moderately well to adsorption. In this formula, x represents the weight of gas or vapor adsorbed by m units by weight of solid; p is the partial pressure of the gas or vapor in question after equilibrium has been reached, and a and n are experimental constants, n being greater than unity. This formula gives a curve similar to the $B-C$ portion in Figure 10, but starting at the origin, point A , and

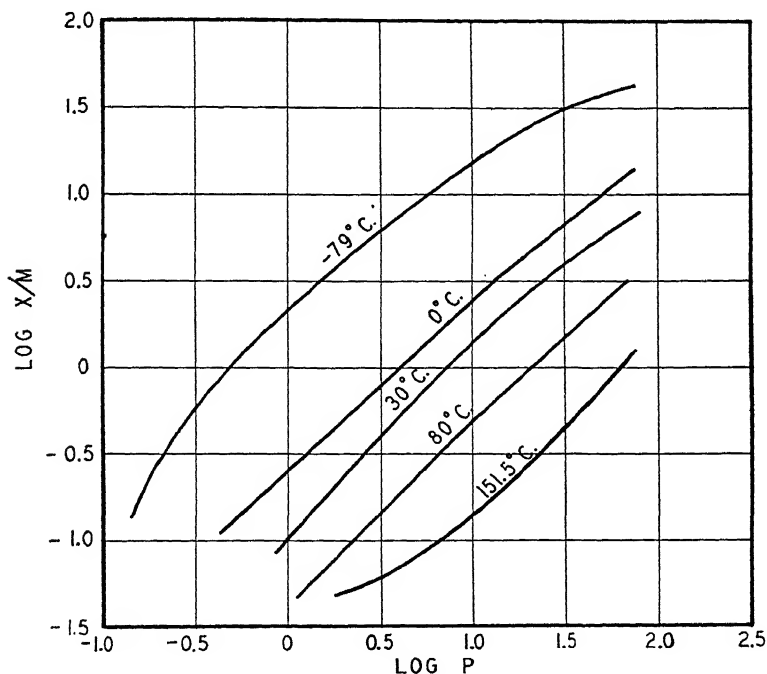


FIGURE 13.

obviously fits only a portion of any actual equilibrium curve. Furthermore, being purely empirical in nature, it offers no picture to explain the phenomenon of adsorption.

A test of its validity is made by plotting the logarithm of x/m against the logarithm of p , since rewriting the formula in its logarithmic form:

$$\log \frac{x}{m} = \log a + \frac{1}{n} \log p$$

gives the equation of a straight line. If the data thus plotted give a straight line, the equation fits. As an example, the data from Titoff³ for nitrogen adsorbed on charcoal, are plotted for several temperatures in Figure 13. This shows that only at one temperature, 0° C., do the data give a straight line. Nevertheless, for many purposes, this approximate formula is very useful on account of its relative simplicity.

Langmuir Monomolecular Formula

A formula has been devised by Langmuir,⁴ based on the assumption that the adsorbed vapor is present on the surface of the solid in a layer one molecule deep and that the greater the fraction of the surface so covered, the less the tendency to accumulate more molecules, and therefore the greater the partial pressure necessary to accomplish such accumulation. This formula is most readily used in the form:

$$(15) \quad \frac{x}{m} = \frac{abp}{1 + ap}$$

where the letters x , m , and p have the same significance as in the Freundlich formula, and a and b are empirical constants which have some connection with the properties of the substances in question.

This formula gives a curve of the same general curvature as the Freundlich formula and fits the same portion, BC , of the equilibrium curve in Figure 10.

In order to test this formula, it may be rewritten:

$$1 + ap = \frac{abp}{x/m}$$

which is the equation of a straight line, where $\frac{p}{x/m}$ is plotted against p . To show this, data on the adsorp-

³ *Z. physik. Chem.*, **74**, 652 (1910).

⁴ *J. Am. Chem. Soc.*, **40**, 1368 (1918).

tion of ethylene, C_2H_4 , by activated sugar charcoal, from McBain and Britton⁵ are plotted this way in Figure 14.

These lines show a satisfactory correlation.

However, plotting the data for water vapor, shown in Figure 11 for activated charcoal and for silica gel, shows that for these cases the formula does not fit well. (Figure 15.)

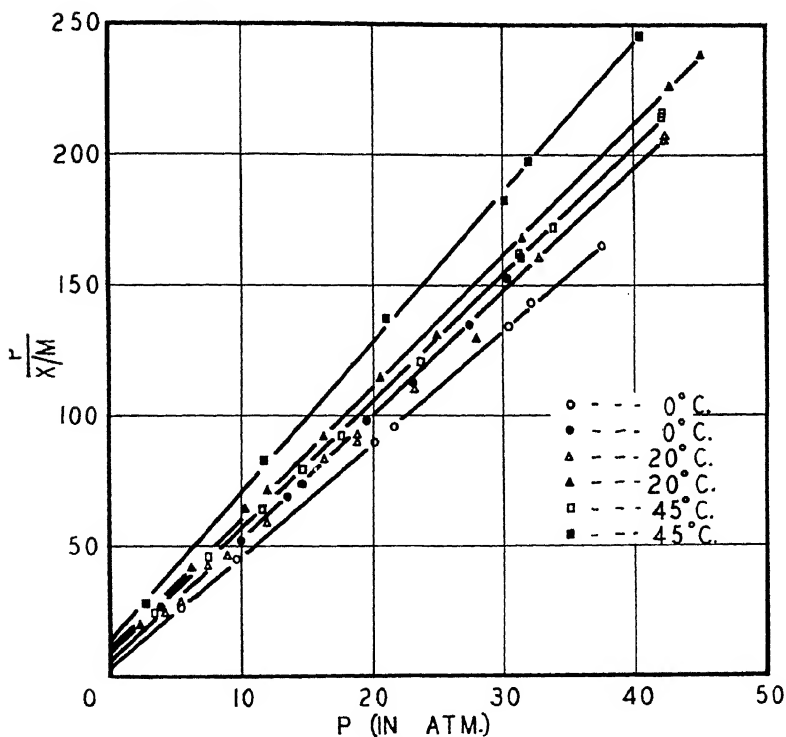


FIGURE 14.

Capillary Adsorption

It is well known that the vapor pressure of a liquid held in a fine capillary is less than that of the same

⁵ *J. Am. Chem. Soc.*, 52, 2218 (1920).

liquid at the same temperature when exposed in large bulk, due to surface tension effects. Under proper surface conditions, therefore, it might be possible for actual liquid to appear in surface capillaries and remain

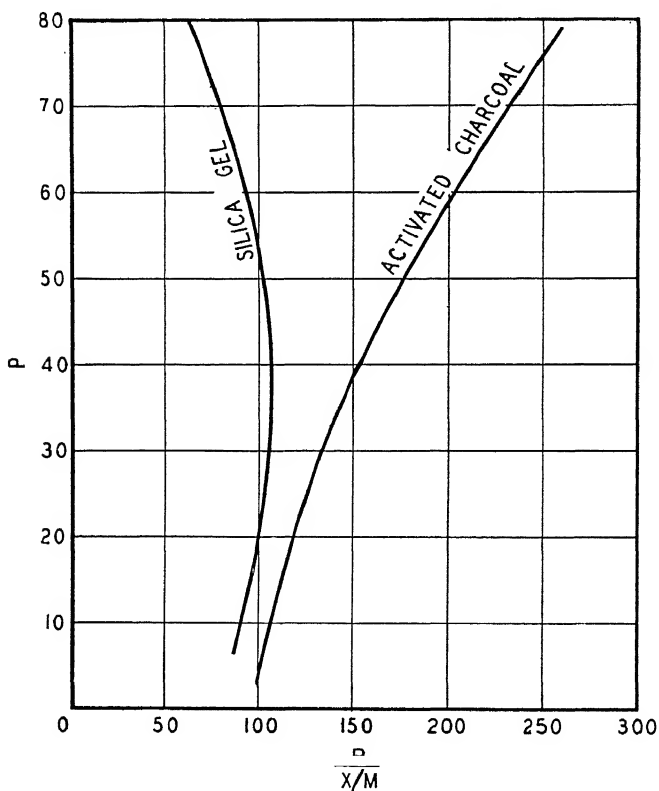


FIGURE 15.

in equilibrium with vapor whose partial pressure is far below that of bulk liquid at that temperature. The small size of the capillaries in adsorbing agents prevents their being seen under a microscope, but some of the effects observed can be readily explained if looked at from this standpoint. For instance, in solids such as silica gel, which appear to depend for their adsorptive

power largely on capillary condensation, it is apparently true that when the partial pressure of the vapor in equilibrium with the solid equals the saturation pressure, the volume of vapor adsorbed, measured as liquefied vapor, is independent of the nature of the vapor, a condition which might easily be explained by assuming the capillaries to have become full, when further adsorption would cease.

The problem is further complicated by variation in the size of the capillaries. The increase in the capacity of solids with increasing partial pressure of the vapor may be explained by the supposition that the smaller capillaries fill up first under lower partial pressures, when the surface tension effects would be greater, while the larger capillaries fill afterward when the pressure is increased.

Patrick Adsorption Equation

The relation between the amount of vapor adsorbed and the partial pressure for solids of the silica gel type has been the subject of work by Patrick and others.⁶ They have found that a modified form of the Freundlich adsorption equation, $\frac{x}{m} = ap^{1/n}$; can be made to fit adsorption by silica gel with considerable precision. This modification has the form:

$$(16) \quad V = K \left(\frac{p\sigma}{P} \right)^{\frac{1}{n}}$$

where V is the volume of the condensed vapor measured as liquid per unit weight of adsorbing solid, p the partial pressure of the adsorbed vapor in equilibrium with the solid, P is the vapor pressure of the liquid at that temperature, σ is the surface tension of the liquid at that temperature, and K and n are constants independent of the nature of the vapor, and dependent only on the physical characteristics of the adsorbing solid.

⁶ *J. Am. Chem. Soc.*, 42, 946 (1920).

Adsorption of Sulphur Dioxide by Silica Gel

The results of some experiments by Patrick, *et al.*, on the adsorption of sulphur dioxide (SO_2) by silica gel (specially prepared $\text{SiO}_2 \cdot n\text{H}_2\text{O}$) are given in the table

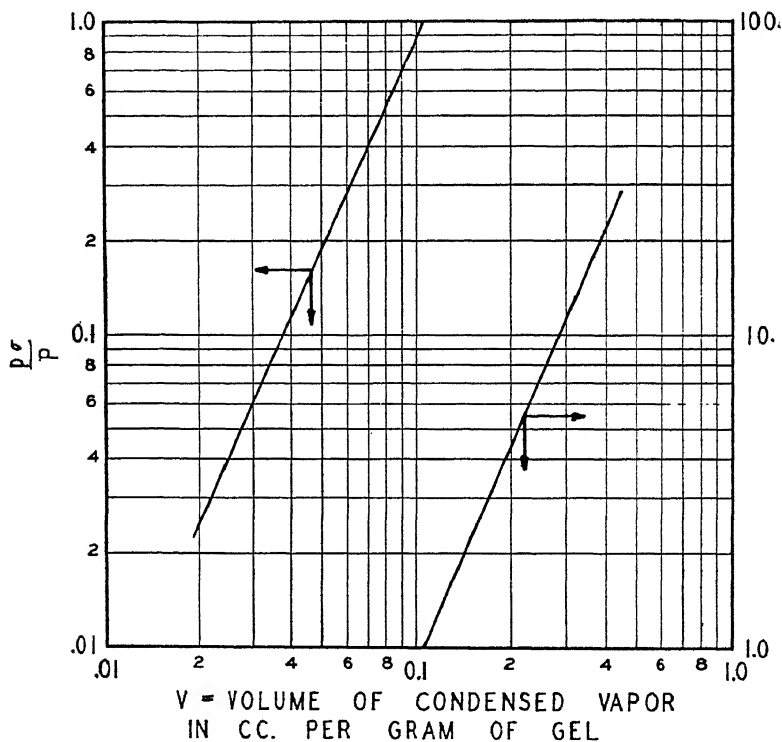


FIGURE 16.

on page 57. The SO_2 used was free from all other gases and vapors.

These data have been plotted in the diagram in Figure 16, on logarithmic paper, plotting $\frac{p^\sigma}{p}$ against V , the former scale having been folded in order to get all

Adsorption of Sulphur Dioxide by Silica Gel

Exp. No.	$t^{\circ}\text{C.}$	c.c. SO ₂ gas adsorbed per gm. gel.	p Partial pres- sure SO ₂ in mm.	P Vapor pressure SO ₂ at t° in mm. Hg.	D Density of liquid SO ₂ at t°	σ Surface tension of liquid SO ₂ at t°	$\frac{p\sigma}{P}$	V vol. SO ₂
XII	100°	12.04	229.9	21143.	1.111	9.25	.1007	.031
	100	17.78	397.0	21143.	1.111	9.25	.1738	.0457
	100	21.99	544.2	21143.	1.111	9.25	.238	.0566
	100	24.65	671.5	21143.	1.111	9.25	.284	.0634
XIX	80	16.73	192.19	13680.	1.192	13.1	.184	.0401
	80	18.66	224.73	13680.	1.192	13.1	.215	.0446
	80	27.70	407.88	13680.	1.192	13.1	.390	.0663
	80	34.17	575.32	13680.	1.192	13.1	.551	.0818
	80	37.41	671.95	13680.	1.192	13.1	.644	.0897
XVIII	40	7.50	9.44	4712.	1.3111	21.0	.042	.0163
	40	16.40	31.37	4712.	1.3111	21.0	.140	.0357
	40	25.25	64.77	4712.	1.3111	21.0	.289	.0550
	40	33.66	110.00	4712.	1.3111	21.0	.490	.0733
	40	41.88	189.13	4712.	1.3111	21.0	.843	.0913
	40	55.54	299.78	4712.	1.3111	21.0	1.338	.1210
	40	75.07	567.52	4712.	1.3111	21.0	2.533	.1635
	40	82.16	692.20	4712.	1.3111	21.0	3.09	.1788
XXIII	40	67.17	448.60	4712.	1.3111	21.0	2.00	.1462
	30	11.85	9.50	3496.	1.3556	22.75	.062	.0250
	30	25.72	40.56	3496.	1.3556	22.75	.264	.0543
	30	36.51	82.32	3496.	1.3556	22.75	.536	.0770
	30	47.77	141.46	3496.	1.3556	22.75	.921	.1007
	30	61.33	241.77	3496.	1.3556	22.75	1.573	.1293
	30	77.52	408.02	3496.	1.3556	22.75	2.66	.1635
	30	91.65	572.10	3496.	1.3556	22.75	3.855	.1933
XXIV	30	99.29	702.40	3496.	1.3556	22.75	4.57	.2093
	0	31.47	10.43	1162.	1.435	28.5	.256	.0627
	0	49.60	31.83	1162.	1.435	28.5	.781	.0988
	0	67.94	67.47	1162.	1.435	28.5	1.645	.1353
	0	80.91	105.35	1162.	1.435	28.5	2.58	.1611
	0	92.89	147.05	1162.	1.435	28.5	3.605	.1851
	0	103.55	190.59	1162.	1.435	28.5	4.67	.2062
	0	116.60	245.57	1162.	1.435	28.5	6.01	.2321
	0	128.47	310.58	1162.	1.435	28.5	7.62	.256
	0	139.03	366.57	1162.	1.435	28.5	8.98	.277
	0	156.79	467.79	1162.	1.435	28.5	11.47	.312
	0	173.82	585.96	1162.	1.435	28.5	14.36	.346
	0	185.18	720.15	1162.	1.435	28.5	17.66	.3685
	0							
XXIX	-34.4	53.31	4.22	232.6	1.5302	36.2	.66	.0995
	-34.4	81.50	13.85	232.6	1.5302	36.2	2.16	.152
	-34.4	108.18	29.02	232.6	1.5302	36.2	4.52	.202

Exp. No.	t° C.	c.c. SO ₂ gas adsorbed per gm. gel.	p Partial pres- sure SO ₂ in mm.	P Vapor pressure SO ₂ at t° in mm. Hg.	D Density of liquid SO ₂ at t°	σ Surface tension of liquid SO ₂ at t°	$\frac{p\sigma}{P}$	V vol. SO ₂
	-34.4	137.17	50.07	232.6	1.5302	36.2	7.78	.256
	-34.4	162.60	73.45	232.6	1.5302	36.2	11.43	.304
	-34.4	192.06	116.62	232.6	1.5302	36.2	18.12	.359
	-34.4	206.50	205.59	232.6	1.5302	36.2	31.95	.386
XXVI	-54	31.19	0.40	88.3	1.565	39.0	.177	.057
	-54	80.00	4.16	88.3	1.565	39.0	1.84	.146
	-54	110.47	9.85	88.3	1.565	39.0	3.91	.202
	-54	143.19	17.55	88.3	1.565	39.0	7.75	.262
	-54	170.93	27.50	88.3	1.565	39.0	12.15	.312
	-54	207.89	44.70	88.3	1.565	39.0	19.75	.389
XXV	-80	50.30	0.13	8.8	1.6295	44.5	.66	.088
	-80	98.82	0.58	8.8	1.6295	44.5	2.93	.173
	-80	145.82	1.65	8.8	1.6295	44.5	8.34	.259
	-80	181.84	3.05	8.8	1.6295	44.5	15.4	.319
	-80	206.67	4.60	8.8	1.6295	44.5	23.25	.362
	-80	229.83	8.30	8.8	1.6295	44.5	41.9	.403

the points on one plot. The lower line is therefore a direct continuation of the upper end of the upper line. The fact that these data approximate a straight line indicated the reliability of the empirical equation (16), since it may be written in the logarithmic form as follows:

$$(17) \quad \log V = \log K + \frac{1}{n} \log \frac{p\sigma}{P}$$

which is the equation of a straight line.

From this line the values of K and $\frac{1}{n}$ were found to be 0.1038 and 0.447 respectively. These values are of course applicable only to the particular sample of silica gel which was used in the experimental work.

Use of Patrick's Equation

Knowing the constants K and $\frac{1}{n}$ for any particular adsorbing agent of this type, it is possible by means of equation (17) to predict the volume of condensed

vapor of any sort whatever which can be adsorbed by the particular solid under specified conditions of partial pressure and temperature.

Example 15. Silica gel is in contact with pure SO_2 gas at 30°C . When equilibrium is reached, the partial pressure of the gas is found to be 600 mm. Using the constants obtained by Patrick, calculate the weight of gel which would be required to adsorb 100 pounds of SO_2 .

Data:

$$\log V = \log 0.1038 + .447 \log \frac{p\sigma}{P}$$

where $p = 600$, $P = 3496$, and $\sigma = 22.75$

$$\log V = \log 0.1038 + .447 \log$$

$$\log V = -.984 + .447 \times .591 = -.720$$

$$V = 0.191 \text{ cc. of liquid } \text{SO}_2 \text{ per gm. of gel.}$$

The density of liquid SO_2 at 30°C . = 1.3556

$$0.191 \times 1.3556 = 0.259 \text{ gm. } \text{SO}_2 \text{ per gm. gel}$$

$$\text{or } 25.9 \text{ lbs. } \text{SO}_2 \text{ per 100 lbs. gel}$$

$$\frac{100 \times 100}{25.9} = 386 \text{ lbs. gel to adsorb 100 lbs. } \text{SO}_2$$

Example 16. Suppose the residual gas from Example 15, amounting to 100 pounds of SO_2 at 600 mm. pressure and 30°C . is removed from the gel, and brought into contact with 100 pounds of fresh gel in a closed tank, at constant pressure. Calculate the weight of SO_2 which would now be adsorbed, and the resulting partial pressure of the gas.

Data:

$$\log V = \log 0.1038 + .447 \log \frac{p \times 22.75}{3496}$$

Basis of calculation: 1 gm. gel and 1 gm. SO_2

$$1 \text{ gm. } \text{SO}_2 = \frac{1}{1.3556} = 0.738 \text{ cc. liquid } \text{SO}_2$$

let

$$x = \text{weight of } \text{SO}_2 \text{ adsorbed}$$

$$1 - x = \text{weight of } \text{SO}_2 \text{ left in gas}$$

then

$$\frac{1 - x}{1} = \frac{p}{600}, \text{ where } p \text{ is the final gas pressure}$$

or

$$p = 600(1 - x)$$

$$\frac{x}{1.3556} = \text{cc. liquid } \text{SO}_2 \text{ adsorbed} = V$$

$$\text{then } \log \frac{x}{1.3556} = -.984 + .447 \log \frac{600(1 - x)(22.75)}{3496}$$

This reduces to the form

$$\frac{x}{\dots} = 0.258$$

The value of x can be obtained by successive approximations, substituting different values for x and calculating the corresponding values of the left-hand side of the equation, until it equals 0.258. The value of x thus obtained was 0.23.

The principal difficulty with correlating experimental data lies in the fact that adsorption is a surface phenomenon, and the amount of vapor adsorbed depends on the amount of surface exposed. There is no satisfactory method for determining the surface of such solids as charcoal, gels, and similar materials, the present methods making use of some relationship such as the heat evolved when the solid is wet by a liquid. For example, Bartell and Fu⁷ found that activated sugar charcoal had a surface of over 600,000 square meters per kilogram, or about 70 acres per pound. Since, however, it is practicable to report the amount of vapor adsorbed only on the basis of the weight of the solid and not on the surface, and since no two batches of solid have the same surface per unit weight, a comparison of adsorption data becomes only semi-quantitative.

For example, the data in the following table were taken from Gregg⁸; they give the amount of gas, measured in cubic centimeters at standard conditions (0° C. and 760 mm. Hg) adsorbed by one gram of charcoal at 0° C. when the partial pressure of the gas was 500 mm. This table gives also the critical temperature and the critical pressure of each gas, and their reduced temperature ($T_R = T/T_C$) and reduced pressure ($P_R = P/P_C$), and the product of the cc. adsorbed multiplied by T_R and P_R . It will be seen that the value for each of these gases is not far from the average value, 0.53, but there is no systematic variation.

⁷ "Colloid Symposium Annual," Johns Hopkins, 7, 138 (1929-30).

⁸ "The Adsorption of Gases by Solids," p. 8, London, 1934.

Gas adsorbed in cc. (s.c.)/gm. charcoal, $t = 0^\circ \text{C.}$, $p = 500 \text{ mm.}$
(.658 atm.)

Substance	Formula	cc/gm	$T_0^\circ \text{K.}$	$P_0 \text{ atm}$	T_R	P_R	$\text{cc} \times T_R \times P_R$
Ammonia	NH_3	138	405.	111.5	.675	.0059	.55
Sulphur dioxide	SO_2	89.3	430.	77.7	.635	.0085	.48
Ethane	C_2H_6	63.1	305.	48.	.895	.0137	.77
Nitrous oxide	N_2O	59.7	310.	71.7	.880	.00918	.48
Acetylene	C_2H_2	59.0	309.	62.	.883	.0106	.55
Carbon dioxide	CO_2	52.5	304.	73.	.898	.0111	.52
Ethylene	C_2H_4	50.8	283.	51.	.965	.0129	.63
Carbon monoxide	CO	10.6	133.	34.5	2.05	.0191	.42
Nitrogen	N_2	7.6	126.	33.5	2.17	.0196	.32
Hydrogen	H_2	1.2	33.3	12.8	8.21	.0504	.50
Average							.53

That this method of using the reduced temperature and pressure for correlating adsorption data can be used only in special cases is shown by the following table, data from McBain,⁹ on the adsorption of gases at 15°C. , by Kahlbaum's Activated Charcoal. The product of the cc. adsorbed by the reduced temperature and the reduced pressure does not give a common value, but values which when plotted as shown in Figure 17 show a gradual trend only.

Gas	Formula	cc/gm at 15°C.	$T_0^\circ \text{K.}$	$P_0 \text{ atm}$	T_R	P_R	$\text{cc} \times T_R \times P_R$	log. cc.
Phosgene	COCl_2	440.	456.	56.	.63	.0179	5.0	2.64
Sulphur dioxide	SO_2	379.7	430.	77.7	.67	.0129	3.3	2.57
Methyl chloride	CH_3Cl	277.0	416.	65.8	.69	.0152	2.9	2.44
Chlorine	Cl_2	234.6	417.	76.1	.69	.0131	2.1	2.37
Ammonia	NH_3	180.9	405.	111.5	.71	.0090	1.16	2.56
Hydrogen sulphide	H_2S	98.9	373.	88.9	.77	.0113	.86	1.995
Hydrogen chloride	HCl	72.0	325.	81.6	.89	.0122	.78	1.86
Nitrous oxide	N_2O	54.2	310.	71.7	.93	.0139	.70	1.73
Acetylene	C_2H_2	48.9	309.	62.	.93	.0161	.73	1.69
Carbon dioxide	CO_2	47.6	304.	73.	.95	.0137	.62	1.68
Methane	CH_4	16.2	191.	45.8	1.51	.0179	.43	1.21
Carbon monoxide	CO	9.3	133.	34.5	2.16	.0290	.58	.97
Oxygen	O_2	8.2	154.	49.7	1.87	.0201	.31	.91
Nitrogen	N_2	8.0	126.	33.5	2.28	.0298	.54	.90
Hydrogen	H_2	4.7	33.3	12.8	8.66	.0782	.32	.67

⁹ "The Sorption of Gases and Vapors by Solids," p. 102, London, 1932.

However, if the logarithm of the cc. adsorbed per gram is plotted against the reduced temperature as shown in Figure 18, a very satisfactory correlation is given, quite adequate for purposes of design.

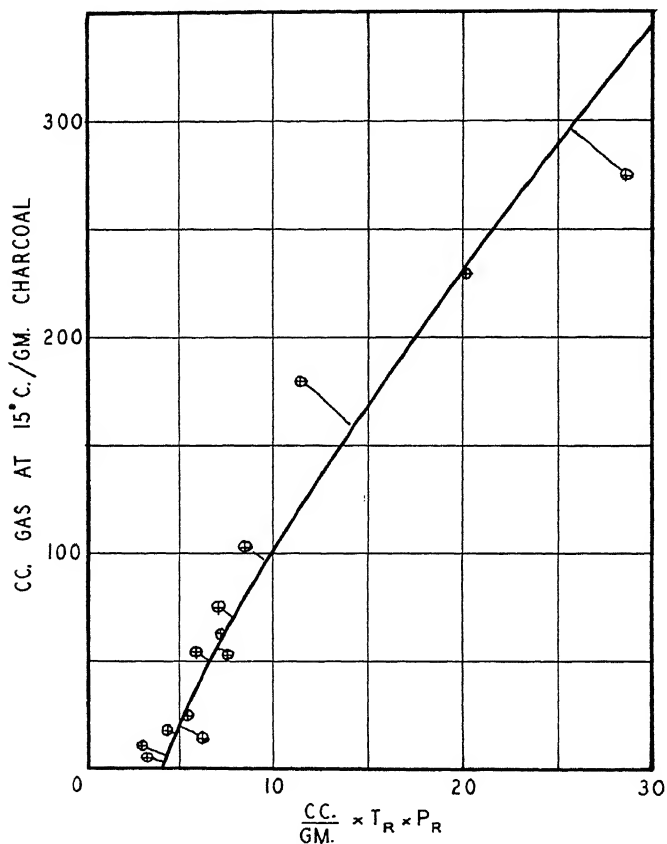


FIGURE 17.

Effect of Temperature on Adsorption

The effect of temperature on the adsorption of vapors by solids is very marked, the amount adsorbed decreasing rapidly with rise in temperature. The fol-

lowing table from Gregg¹⁰ shows the amount of ethylene adsorbed by charcoal at a constant partial pressure of 30 centimeters of mercury at several temperatures. the amount adsorbed being expressed in cc. at standard conditions per gram of charcoal.

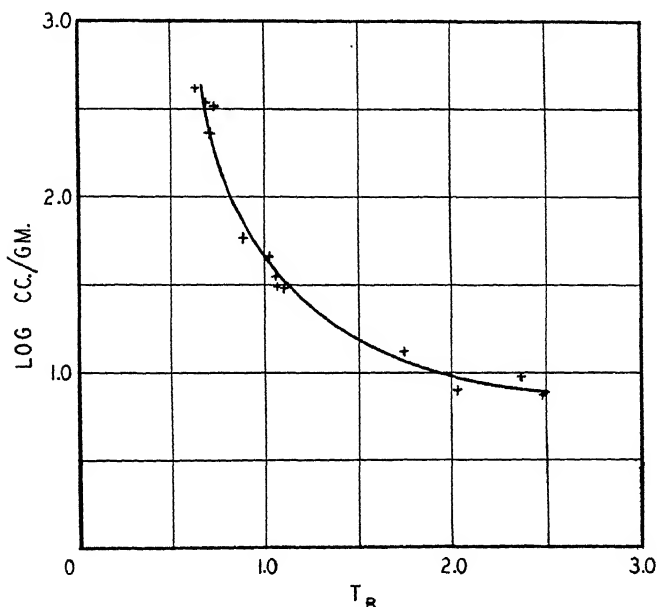


FIGURE 18.

cc./gm	T° C.	T° K.	T_R	log (cc./gm)
154	0	273	.964	2.19
127	20	293	1.035	2.10
77	40	313	1.105	1.89
43	100	373	1.317	1.63
10	182	455	1.607	1.00

If the logarithm of the cc./gram is plotted against the reduced temperature (T_R), it is seen that there is an excellent correlation. (Figure 19, curve A.)

¹⁰ "The Adsorption of Gases by Solids," Table 3, page 8.

THE RECOVERY OF VAPORS

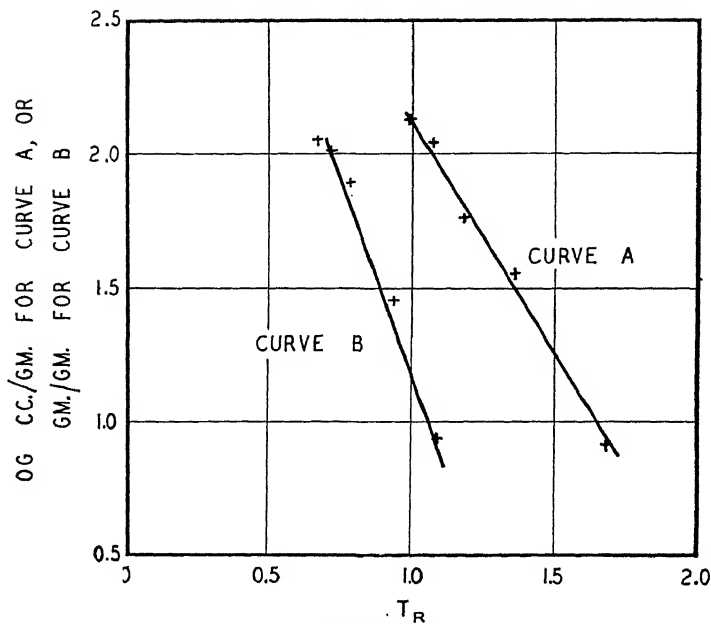


FIGURE 19.

Similarly the adsorption of NH_3 ¹¹ is given in the following table for ammonia on charcoal at a partial pressure of 70.5 cm. of Hg.

$\left(\frac{x}{m}\right)$ gm NH_3 / gm. charcoal	$T^\circ \text{C.}$	$T^\circ \text{K.}$	T_R	$\log \left(\frac{x}{m}\right)$
155.6	-23.5	249.5	.616	2.19
134.6	0	273	.674	2.13
97.27	30	303	.748	1.987
36.14	80	353	.872	1.56
10.26	151.5	424.5	1.048	1.01

The logarithm of $\frac{x}{m}$ is plotted against T_R as Curve B in Figure 19, showing a reasonably satisfactory correlation.

¹¹ Titoff, *Z. physik. Chem.*, 74, 674 (1910).

Heat of Adsorption

A very large amount of heat is liberated when vapors condense, either into the liquid condition or into a film adsorbed on the surface of solids. This heat is called the latent heat of condensation or adsorption, as the case may be, and is usually expressed as calories per gram, or as British thermal units per pound. In most cases, the value for adsorption is much larger than for condensation into the liquid condition, but it varies considerably depending on the partial pressure of the gas in contact with the solid: the lower the pressure, the higher the heat of adsorption. Furthermore, the heat liberated in adsorption varies with the amount already adsorbed by a given sample of solid, so that the total heat evolved is the sum or integral of all the variable amounts.

Gregg¹² gives the differential heat of adsorption, $\left(\frac{dQ}{dx}\right)$, expressed in calories per gram mol (molecular weight in grams) for the range in partial pressures noted. The corresponding latent heat of condensation is also given in corresponding units.

Gas Charcoal as adsorbent	Formula	T° C.	Differential Heat dQ/dX	Partial Pressure Range (mm.)	Latent Heat at 0° C.
Nitrogen	N ₂	0	6410-4790	11.1- 75.0	
Hydrogen	H ₂	40	3310-3180	19. -727	
Nitrous oxide	N ₂ O	0	7870-7020	0 -728	2510
Ethylene	C ₂ H ₄	10	8900-7100	0 -550	2050
Acetylene	C ₂ H ₂	0	9210-7370	0 -822	2580
Carbon dioxide	CO ₂	0	7770-6120	0 -450	2570
Sulphur dioxide	SO ₂	0	11,800-8770	0 -838	5980
Water	H ₂ O	10	11,400-9490	0 - 16.8	10,440

Approximate values for the above may be calculated by means of the Clapeyron Equation (see Chapter 3) when actual values are not available, if x/m is available for various pressures and temperatures.

Lamb and Coolidge¹³ give a formula for calculating

¹² "The Adsorption of Gases and Solids," Table 8, page 37.

¹³ *J. Am. Chem. Soc.*, **42**, 1146 (1920).

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the total or integral heat of adsorption for a number of vapors adsorbed on steam-activated coconut charcoal.

This formula is $q = ax^b$ where q = calories evolved by x cc. (at s. c.) of vapor adsorbed on 1 gram of charcoal, a and b being empirical constants. The column marked q' is the value of q when x corresponds to 1 gram mol on 500 grams of charcoal, while ρ is the latent heat of condensation to the liquid condition for one mol.

Substance	Formula	a	b	q'	ρ
Ethyl chloride	C_2H_5Cl	0.7385	0.915	12,000	6,220
Carbon disulphide	CS_2	0.7525	0.9205	12,500	6,830
Methyl alcohol	CH_3OH	0.742	0.938	13,100	9,330
Ethyl bromide	C_2H_5Br	0.900	0.900	13,900	6,850
Ethyl iodide	C_2H_5I	0.737	0.956	14,000	7,810
Chloroform	$CHCl_3$	0.8285	0.935	14,500	8,000
Ethyl formate	$HCOOC_2H_5$	0.944	0.9075	14,500	8,380
Benzene	C_6H_6	0.774	0.959	14,700	7,810
Ethyl alcohol	C_2H_5OH	0.871	0.928	15,000	10,650
Carbon tetrachloride	CCl_4	0.893	0.930	15,300	8,000
Ethyl ether	$(C_2H_5)_2O$	0.917	0.9215	15,500	6,900

The importance of the heat of adsorption is evident when it is realized that all this heat must be removed from the adsorbing solid in order to avoid any rise in temperature, with a corresponding reduction in adsorbing capacity.

Chapter 9

Adsorption of Mixed Gases

Condensation of Mixed Vapors

Mixtures of gases and vapors, when brought into contact with an adsorbing medium, are not condensed in the same proportion as they exist in the gaseous phase, but in general approximately inversely according to their relative volatilities. A mixture of a very volatile vapor and a slightly volatile one, when brought into contact with an adsorbing agent, will produce a condensed vapor containing a much greater proportion of the less volatile vapor than exists in the gas. An example of this is given by Miller.¹

Mixture of Sulphur Dioxide and Air

Mixtures of SO₂ and air at several temperatures were brought into contact with silica gel, and when saturated, the weight of SO₂ adsorbed per unit weight of gel was determined. At ordinary temperatures, 0° C. to 40° C., the vapor pressure of air is so great that practically none adsorbs in comparison with the SO₂, and such a mixture of air and SO₂ should therefore behave in a similar manner to pure SO₂. The following data were read from plots in Miller's article:

Percentage SO ₂ in Gas	Temp. (°C.)	SO ₂ Adsorbed as % by Weight of Gel	Percentage SO ₂ in Gas	Temp. (°C.)	SO ₂ Adsorbed as % by Weight of Gel
1	30	2.4	1	40	1.6
2	30	3.9	2	40	2.7
3	30	5.1	3	40	3.4
4	30	5.9	4	40	4.1
5	30	6.6	5	40	4.7
6	30	7.2	6	40	5.3
7	30	7.7	7	40	5.8
8	30	8.0	8	40	6.3

Chem. Met. Eng., 23, 1155 (1920).

Equation (16), discussed on page 55, should apply in this case, K and $\frac{1}{n}$ not being known. It is assumed that the total pressure on the mixed gas was 760 mm.

entage in Gas	p (mm.)	P (mm.)	t	V	σ	D	$\frac{p\sigma}{P}$
1	7.6	3496	30	.0177	22.75	1.3556	.0495
2	15.2	3496	30	.0288	22.75	1.3556	.099
3	22.8	3496	30	.0377	22.75	1.3556	.1485
4	30.4	3496	30	.0436	22.75	1.3556	.198
5	30.8	3496	30	.0487	22.75	1.3556	.247
6	45.6	3496	30	.0532	22.75	1.3556	.297
7	53.2	3496	30	.0568	22.75	1.3556	.346
8	60.8	3496	30	.0591	22.75	1.3556	.396
1	7.6	4712	40	.0122	21.0	1.3111	.034
2	15.2	4712	40	.0206	21.0	1.3111	.068
3	22.8	4712	40	.0259	21.0	1.3111	.102
4	30.4	4712	40	.0313	21.0	1.3111	.135
5	38.0	4712	40	.0359	21.0	1.3111	.169
6	45.6	4712	40	.0404	21.0	1.3111	.203
7	53.2	4712	40	.0442	21.0	1.3111	.237
8	60.8	4712	40	.0481	21.0	1.3111	.271

In the above table the symbols have the same meaning as in Chapter 8. V was calculated as follows:

$$V = \frac{2.4}{100} \div 1.3556 = .0177 \text{ cc. liquid SO}_2 \text{ per gm. of gel.}$$

These data have been plotted as before on logarithmic paper, in Figure 20, and the points are found to lie on approximately a straight line as shown. The equation for this particular sample of silica gel would therefore be

$$V = 0.11 \left(\frac{pD}{P} \right)^{.617}$$

as determined by the slope and intercept of the line.

This work indicates that for mixtures of condensable vapors with inert gases, the empirical equation derived by Patrick is sufficiently close to the truth for engineering purposes when used with gels of this type, and in general it may be stated that the presence of air or of an inert gas has practically no effect upon the weight

ADSORPTION OF MIXED GASES

of vapor adsorbed, the chief difference in behavior from a pure vapor being in a much slower rate of adsorption.

Adsorption of Ether and Air

Further work by Miller ² on the adsorption of other vapors from air by silica gel is summarized as follows:

% Ether in Air	t° C.	% Ether Adsorbed by Gel	p (mm.)	P (mm.)	V	D	$\frac{\sigma}{P}$
1.00	25	14.6	7.6	534	.206	16.0	.227
3.08	25	15.7	23.4	534	.221	16.0	.701

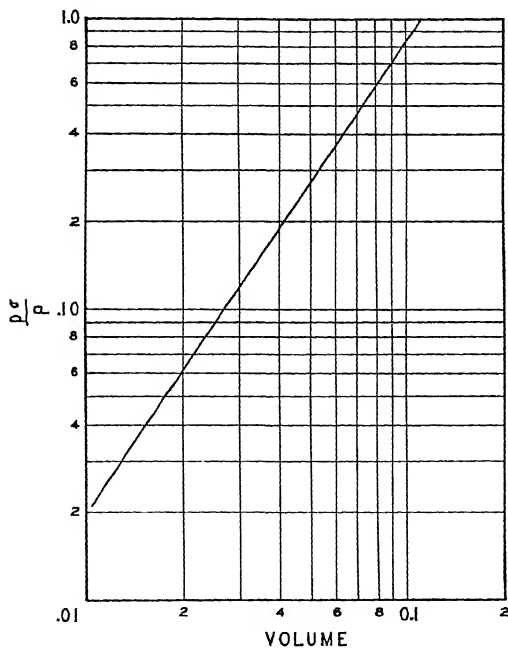


FIGURE 20.

The corresponding values of K and $\frac{1}{n}$ were calculated and found to be .226 and .063 respectively.

² *Chem. Met. Eng.*, 23, 1219 (1920).

Adsorption of Benzene Vapor and Air

% Benzene in Air	t° C.	% Benzene Adsorbed	<i>p</i> (mm.)	<i>P</i> (mm.)	σ	<i>D</i>	$\frac{p\sigma}{P}$	<i>V</i>	<i>V</i> (calc.)	Devia- tion
0.65	25.	15.3	4.9	96	29.5	.873	1.505	.175	.178	+ .003
3.34	25.	19.7	25.4	96	29.5	.873	7.81	.226	.222	— .004
9.00	25.	21.6	68.3	96	29.5	.873	21.0	.247	.252	+ .005

Calculating the average values of K and $\frac{1}{n}$ for these tests, they were found to be as follows:

$$K = 0.170 \qquad \frac{1}{n} = 0.131$$

V was then calculated in each case using these values, and the results are included above, the average deviation being only 0.004.

Adsorption of Water Vapor and Air

t° C.	% Water Adsorbed	<i>p</i> (mm.)	<i>P</i> (mm.)	σ	<i>D</i>	$\frac{p\sigma}{P}$	<i>V</i>	<i>V</i> (calc.)	Devia- tion
30	25.7	31.8	31.8	69.1	.996	69.1	.258	.268	+ .010
30	22.5	16.6	31.8	69.1	.996	36.2	.226	.226	0.
30	15.6	8.5	31.8	69.1	.996	18.5	.156	.190	+ .034

These tests gave $\frac{1}{n} = 0.263$ and $K = .278$ and the calculated values of V were found to deviate from the determined by about 0.014.

Since silica gel is made by the partial dehydration of silicic acid, it would be expected that the adsorption of water vapor on the gel would have more of the character of a chemical affinity and less of capillary condensation, than would be the case in the adsorption of hydrocarbons, for instance, for which there would be little molecular attraction. It would therefore be expected that the gel would deviate from the Patrick equation in the case of water. The foregoing data show this to be true.

Adsorption of Mixed Vapors from Gases

The adsorption of mixed vapors from air or from an inert gas, while following the same general rules as the

single vapors, is complicated by the selective action of the adsorbing medium. When air containing a mixture of substances of varying volatility is brought into contact with the adsorbing medium, the more volatile as well as the less volatile vapors are readily adsorbed at

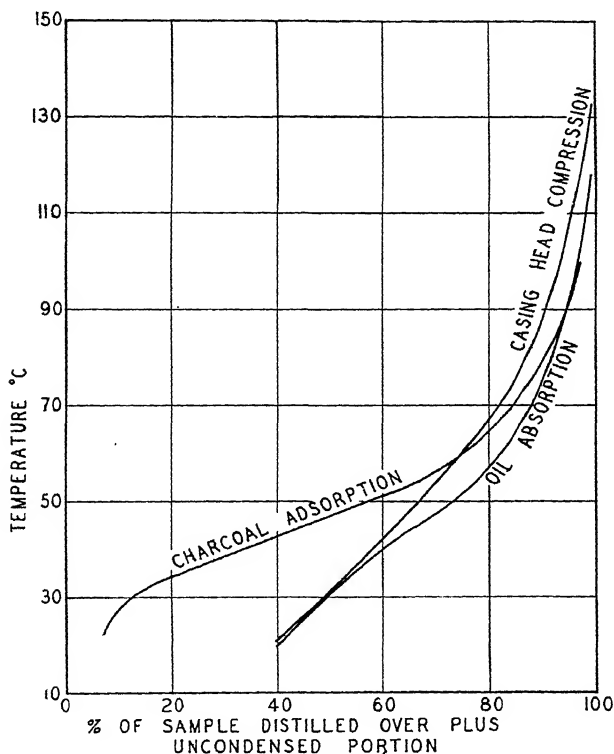


FIGURE 21.

the start; but as the solid approaches saturation, the more volatile vapors revaporize as the less volatile condense, so that when equilibrium is reached, the adsorbed vapor consists largely of the less volatile constituents. Tests made by Burrell and others³ on the adsorption of mixed gasoline vapors from natural gas

³ *Chem. Met. Eng.*, 24, 156 (1921).

show this selective effect very clearly. The diagram,⁴ Figure 21, shows the Engler distillation curves of such gasoline obtained from the same natural gas by compression, oil absorption, and by adsorption on active carbon. It will be seen that the last contains much less very volatile material than either of the others. The first portions of all the samples were so volatile that they were uncondensed on Engler distillation.

⁴Reconstructed from *Chem. Met. Eng.*, 24, Fig. 6, 159 (1921).

Chapter 10

Rate of Adsorption

The rate of adsorption of a vapor by a solid is proportional to the difference between the partial pressure of the vapor in the gas in contact with the solid and the partial pressure of the condensed vapor actually present on the surface of the solid at the same time. Thus, at the start of the adsorption, if the solid is free of condensed vapor, the rate of adsorption is a maximum, usually very great. As soon as any vapor has condensed, however, the rate of adsorption will decrease until, when the solid has become saturated with the vapor, the vapor pressure will equal the partial pressure and adsorption will cease. The mathematical analysis of the rate of adsorption for vapors on solids is difficult, involving differentials of the second order. Those interested can find a discussion of the analysis in an article by W. K. Lewis.¹

Canister Test

Considerable work is available in the literature regarding the rate of adsorption. In general, tests have been made by passing gases of known concentration at specified rate of flow and at constant temperature through a known mass of the adsorbent. The action of the adsorbent on the gas can be illustrated by Figure 22.

In this diagram the rectangle represents a box filled with adsorbent, with gas carrying adsorbable vapor travelling from left to right. The horizontal coördinate represents the length of the box l , and the vertical coördinate, the partial pressure of the vapor in the

¹"The Principles of Counter-current Extraction," *J. Ind. Eng. Chem.*, 8, 825 (1916).

gas, p . At the start, when no vapor has entered the box, the partial pressure of the vapor is p_0 . The vapor then coming in contact with fresh adsorbent is rapidly condensed in passing through the box, the partial pressure decreasing along the curve $p_0 a l_1$. At l_1 the curve becomes practically tangent to $p=0$, and therefore beyond that point the gas contains practically no vapor.

The solid at the entrance end soon adsorbs enough vapor to reduce its adsorbing capacity, and therefore

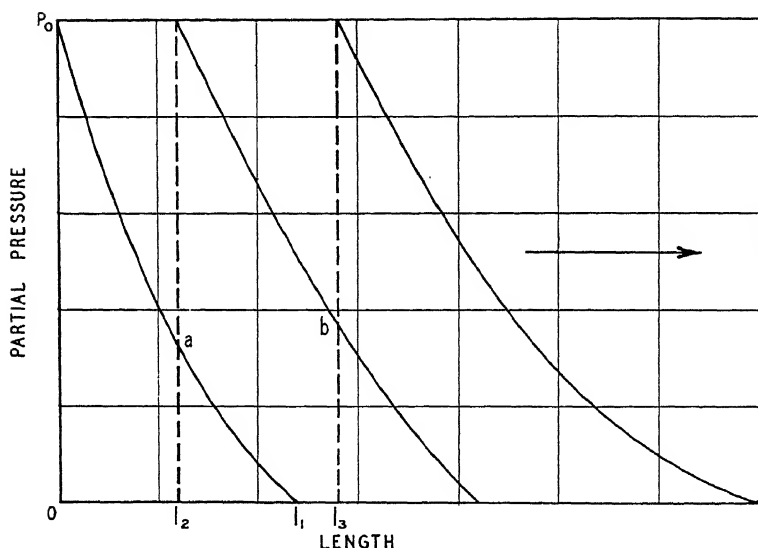


FIGURE 22.

after a short time will be saturated with respect to the entering vapor as far as the point l_2 , the vapor condensing in a new curve b , at that time. The saturation of the solid will proceed, until the time is reached when the solid has been saturated as far as the point l_3 and the partial pressure curve reaches $p=0$ at the right-hand end of the diagram. At this time appreciable amounts of uncondensed vapor will start to leave the

apparatus with the exit gases. This point is known as the "break point" of the sample. Further flow through the apparatus will increase the partial pressure in the exit gas until finally the partial pressure will be the same as that in the entering gas, when no more vapor can be adsorbed and the solid is saturated throughout for that particular set of conditions of partial pressure and temperature.

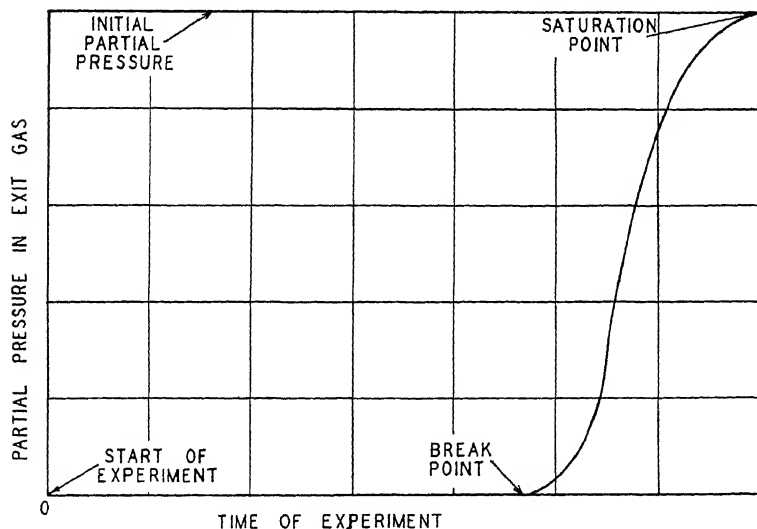


FIGURE 23.

This progressive saturation of an adsorbent can be shown by a diagram as given in Figure 23.

Adsorption by Activated Carbon

A number of tests of adsorptive capacity for various materials have been made. The following are taken from an article on "Gas Mask Absorbents," by Lamb, Wilson and Chaney.²

² *J. Ind. Eng. Chem.*, 11, 420 (1919).

Tests on Activated Carbon

Source	Time of Activation with Steam at 900° C. (min.)	% Weight Adsorbed	Time (min.)
Sycamore	18	41	7.3
Cedar	60	78	16.0
Mountain mahogany	60	32	16.3
Ironwood	60	31	20.8
Brazil nut	120	46	32.2
Ivory nut	120	48	47.0
Cohune nut	120	51	53.4
Babassu nut	210	85	58.7
Coconut	120	61	58.7
Coconut	180	72	64.4
Briquetted sawdust	120	53	40.0
Briquetted carbon black	240	53	50.5
Briquetted bituminous coal	165	58.3	46.8
Briquetted anthracite	480	53	40.7

These tests were made by passing dry air containing 7500 parts per million of chlorpicrin [$C(NO_2)Cl_3$] at the rate of 1000 cc. per minute through a tube containing the carbon, 1.41 cm. inside diameter and 10 cm. long. The time recorded was the number of minutes before chlorpicrin appeared at the exit end in concentration greater than 1% of the entering concentration, that is, 75 parts per million, corresponding practically to the break point in Figure 23.

Another set of tests given in the same article indicates the adsorptive values of different dry carbons against various gases.

Conditions of Tests

Vapor concentration	0.1%
Mesh of adsorbent	8 to 14
Depth of adsorbent	10 cm.
Rate of flow per sq. cm. per min.	500 cc.
Relative humidity of air	50%
Temperature	20° C.

Typical Adsorptive Values of Different Carbons Against Various Gases

Times (in minutes) Corrected to 99% Efficiency of Adsorption.

		mpie			Air	Cyanogen Chloride	lor- ylchlor- ate
Poor U. S. coconut	270*	120*	175*	20*	18*	56*	50*
Medium U. S. coconut	370	350	260	25	25	65	65
Good U. S. coconut	420	620	310	27	30	75	70
Wood charcoal, French		25	75	9	0	1	20
Wood charcoal, British		70	90	18	4	5	30
Peach stone		190	135	30	25	65	60
Treated wood, German		230	105	20	20	22	25

* All values represent time in minutes.

Further tests on the adsorption of gases by charcoal are given by Harned.³ These tests show the effect of the method of preparation of the carbon on the adsorptive capacity.

Adsorption by Silica Gel

Tests were made by Miller⁴ on the rate of adsorption of sulphur dioxide from dry air at 20° C. In these tests the rate of flow was 200 cc. per square centimeter per minute through 5 grams of gel, cross-section of flow 3 square centimeters (Figure 24).

Similar tests^{4a} were made on the adsorption by silica gel of ether, acetone, benzene, water vapor and gasoline.

Adsorption of Gasoline by Activated Carbon

Some tests on adsorption by activated carbon of gasoline from natural gas are given by Burrell.⁵ Using gas containing 400 gallons of gasoline per million cubic feet, and passing it through a tower 5 feet high at the

³ *J. Am. Chem. Soc.*, 42, 372 (1920).

⁴ *Chem. Met. Eng.*, 23, 1155 (1920).

^{4a} *Chem. Met. Eng.*, 23, 1219 (1920).

⁵ *Chem. Met. Eng.*, 24, 156 (1921).

rate of 40 cubic feet per hour per square inch of base area, the efficiency curve in Figure 25 was obtained.

The adsorption of gasoline is complicated by the fact that it is a mixture of a number of substances of varying vapor pressures. The commercial application is discussed on page 100.

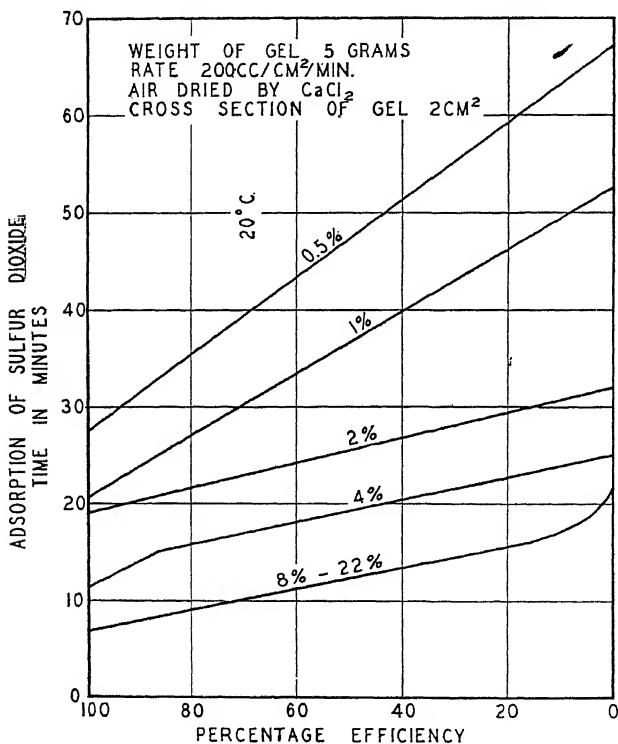


FIGURE 24.

Bohart and Adams Equation

Empirical equations for the rate of adsorption have been derived by Bohart and Adams,⁶ in which c represents the concentration of the vapor which is being

adsorbed at any point during its passage through the adsorbing solid, the distance through which it has passed being x , a being the residual vapor capacity of the solid at any time, and v the rate of flow of vapor per hour expressed in terms of volume of solid saturated per hour if completely saturated.

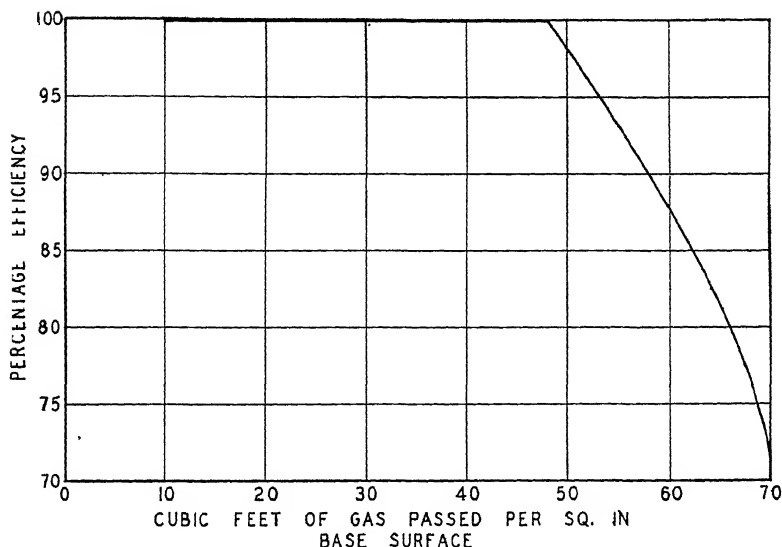


FIGURE 25.

The rate at which the capacity of the solid to adsorb diminishes is indicated by the equation:

$$(18) \quad \frac{\delta a}{\delta \theta} = -kac$$

and the rate at which the gas loses vapor is indicated by the equation:

$$\frac{\delta c}{\delta x} = \frac{-k}{v} ac$$

These equations when combined and integrated gave the following, where c_0 and a_0 represent initial vapor concentration and capacity, respectively:

$$(20) \quad \frac{c}{c_0} = \frac{10^{0.4343kc_0\theta}}{10^{0.4343k\frac{a_0x}{v}} - 1 + 10^{0.4343kc_0\theta}}$$

$$(21) \quad \frac{a}{a_0} = \frac{10^{0.4343k\frac{a_0x}{v}}}{10^{0.4343k\frac{a_0x}{v}} - 1 + 10^{0.4343kc_0\theta}}$$

These equations, while open to criticism on account of the assumptions as to rate of adsorption, give curves which fit the experimental data very well.

For a batch adsorption process where a vapor and solid are brought together at constant temperature, Baugham and others⁷ found that a formula of the following type fitted the data:

$$(22) \quad \log \frac{x_s}{x_s - x} = k\theta^{1/n}$$

where x and x_s are the weights of vapor adsorbed in the time θ and the time infinity respectively, while k and n are empirical constants.

Francis and Burt⁸ found that k increases with rise of temperature, being about doubled with a rise of 20° C. Since, however, x_s decreases rapidly with rise in temperature, the best temperature for adsorption is usually a relatively low one.

Data by Ahlberg,⁹ on the rate of adsorption of water by silica gel give characteristic curves as shown in Figure 26. In these curves, the weight of water adsorbed by a unit weight of gel is plotted against the time in minutes, for an air flow of 168 cubic feet per minute per square foot of tower cross-section, using silica gel of 4-6 mesh and with the temperature and partial pressure of water vapor in the air entering the tower shown on the individual curves. The depth of the gel parallel to the flow of air was one inch. The rate of adsorption may be determined at any instant by

⁷ *Proc. Roy. Soc. London (A)*, 105, 981 (1924).

⁸ *Proc. Roy. Soc. London (A)*, 116, 586 (1927).

⁹ *Ind. Eng. Chem.*, 31, 988 (1939).

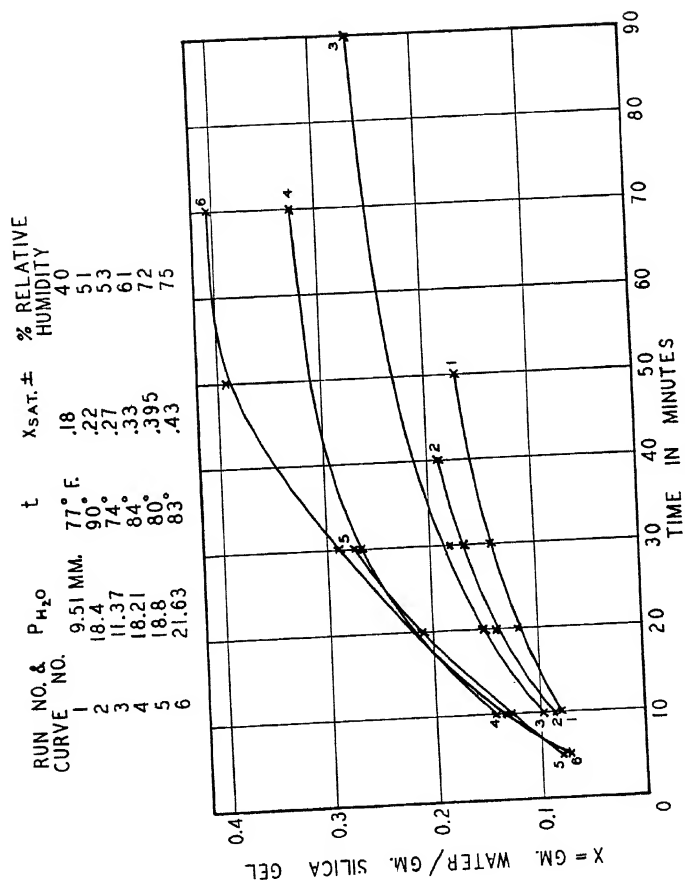


Figure 26.

drawing a line tangent to the curve at that point and measuring its slope, which will give the rate expressed as grams of water vapor adsorbed per gram of gel per minute. Figure 26 uses data from table 5 of the article by Ahlberg.

The adsorption of water vapor from air by silica gel under these conditions is substantially a diffusion process of the water vapor through a more or less stationary layer of air in the surface of the gel which is nearly in equilibrium with it. The rate at which this diffusion takes place, therefore, is proportional to the difference between the partial pressure of the water vapor in the air and that in the film in contact with the solid. One way of expressing this potential or driving force which causes the adsorption to take place is to say that the rate of diffusion is proportional to the tendency of the solid to become saturated with respect to the air blowing by it, and the further it is from the saturation value, the greater the rate. This may be written as a differential equation in the form:

$$(23) \quad \frac{dx}{d\theta} = k(x_s - x)$$

where x represents the amount of water vapor already picked up by the solid at the time θ expressed as grams of water per gram of solid, x_s represents the value of x when it is saturated in respect to the air which is being blown over the gel, and k is a diffusion constant which is likely to increase with rise in temperature.

This equation must be integrated, giving

$$(24) \quad \log_e \frac{x_s - x}{x_s - x_0} = k\theta$$

and when the value of the left-hand side of the equation is divided by the value of θ corresponding to the value of x , a value of k is obtained which should be reasonably constant if the formula fits the data. This has been done as shown in the following table and it will be seen that the value of k for each run is nearly

constant. There seems to be a slight trend for k to increase with temperature, but a considerably greater tendency for it to decrease as the relative humidity of the air increases.

Run	θ		x	$\frac{x_s}{x_s-x}$	$\log_e \frac{x_s}{x_s-x}$	$\frac{1}{\theta} \log_e$	$\frac{x_s}{x_s-x} = k$	k_{average}
1	10	.18	.08	1.80	.587	.587		
	20		.119	2.95	1.080	.540	2.186	
	30		.142	4.74	1.555	.518	<u>4</u>	.547
	50		.168	15.0	2.707	.541		
2	10	.22	.088	1.67	.515	.515		
	20		.142	2.83	1.040	.520	2.017	
	30		.169	4.31	1.460	.492	<u>4</u>	.504
	40		.189	7.10	1.960	.490		
3	10	.27	.097	1.56	.444			
	20		.153	2.31	.837	.429	1.691	
	30		.180	3.00	1.078	.366	<u>4</u>	.423
	90		.264	45.0	3.81	.452		
4	10	.33	.141	1.75	.559	.559		
	20		.211	2.77	1.017	.509	2.192	
	30		.267	5.23	1.653	.551	<u>4</u>	.548
	70		.324	55.0	4.01	.573		
5	5	.395	.079	1.25	.223	.446		
	10		.128	1.48	.392	.392	1.598	
	20		.210	2.13	.755	.378	<u>4</u>	.399
	30		.272	3.21	1.165	.382		
6	5	.43	.077	1.185	.169	.338		
	10		.135	1.46	.378	.378	2.333	
	20		.213	1.98	.682	.341	<u>5</u>	.467
	30		.290	3.07	1.121	.374		
	50		.393	11.6	2.45	.490		
	70		.406	17.9	2.883	.412		

Chapter 11

Recovery of Adsorbed Vapors

Vaporization of Adsorbed Vapor

Adsorbed vapors can be revaporized by bringing into contact with the solid, gas containing the vapor in question at such a concentration that its partial pressure is less than the vapor pressure of the condensed vapor on the solid. The maximum rate of revaporization at a given temperature occurs when the gas contains no vapor whatever. The adsorbed vapors can also be revaporized by raising the temperature of the solid in the absence of any other gas to such a point that the vapor pressure of the adsorbed vapor equals the external pressure, when revaporization will start. In order for it to continue under these conditions, the temperature required for complete revaporization is often very high.

Vaporization of Sulphur Dioxide

Patrick¹ found that the adsorption of air-free SO_2 by silica gel was reversible, and that in the recovery of the SO_2 by revaporization the relations determined in a previous chapter held true. But if other gases are present when the SO_2 is adsorbed, the recovery is no longer reversible, and there is a hysteresis effect, the adsorption and revaporization curves being similar to those in Figure 27.

From this diagram, it is evident that under these conditions, an adsorbing agent in contact with a gas containing a vapor of the partial pressure a , would adsorb b parts of that vapor when equilibrium was

¹ *J. Am. Chem. Soc.*, 42, 963 (1920).

reached; but if the partial pressure is reduced, vaporization does not begin until the partial pressure of the vapor in contact with the solid reaches the value *c*.

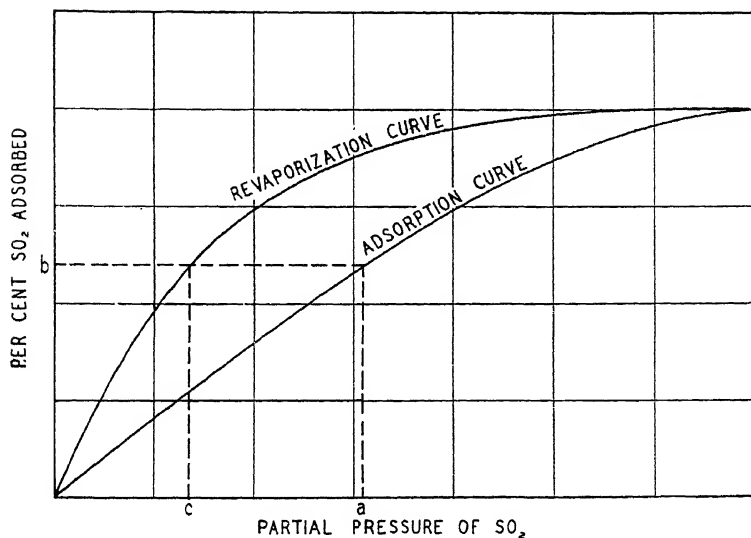


FIGURE 27.

Type of Adsorbing Agent

The effect of the type of adsorbing agent on the recovery of adsorbed vapor is shown in Figure 28.²

This diagram shows the percentage of vapor adsorbed, based on the weight adsorbed at the break-point as 100% when air saturated with chlorpicrin at 0° C. is passed through.

When the break-point was reached, air, free from chlorpicrin, was passed through the solid at the same rate and temperature, the condensed vapor revaporizing as shown, those solids of the capillary condensation type giving up their vapor more readily than the others.

²From R. E. Wilson, verbally.

Of course, raising the temperature would have accelerated this revaporization tremendously.

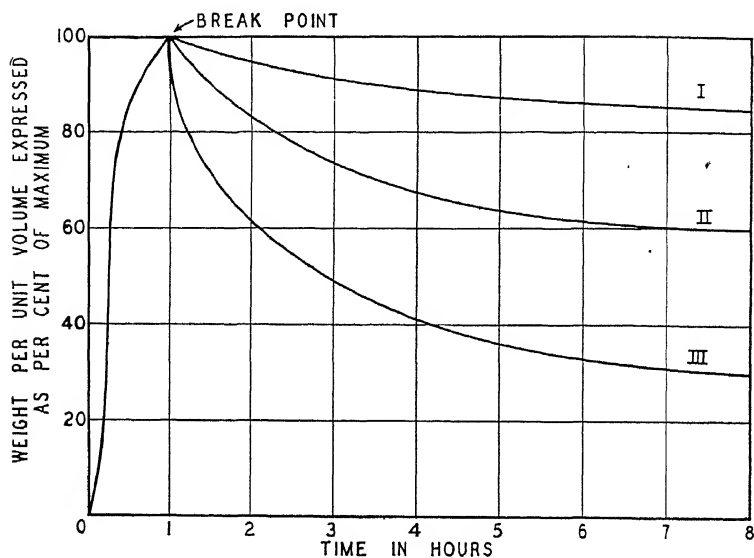


FIGURE 28.

Gas Used in Revaporization

In recovery operations, where a gas is used as a carrier to assist in removing the condensed vapor, the gas may consist either of the so-called permanent gases—air, carbon dioxide, and so forth—or it may consist of some easily condensable vapor, such as steam. In either case, the revaporization can be carried out as indicated above; but when the gas or vapor is cooled afterwards to recover the vapor in liquid form, whether or not an inert gas or vapor was used makes a great difference in the recovery. When steam is used as the carrier gas, it can all be condensed in a suitable condenser, and all the revaporized vapor will condense with it, giving complete recovery of the vapor. But if air or gas is used, cooling will not condense it, and only

a portion of the vapor which it carries will be condensed, the balance, in amount dependent on the vapor pressure and temperature, being rejected with the waste air. Of course, if the air is used over again, this loss can be largely avoided, provided the apparatus has no leaks. It is therefore usual to recover adsorbed vapors by the use of easily condensable vapor, either saturated or superheated, as may be convenient, and the use of inert gas for such purposes is confined almost exclusively to recirculating systems.

Steaming Silica Gel

Experiments by Miller ³ in recovering vapors from silica gel are tabulated below:

Exp. I:

One hundred grams of gel containing 29 grams of adsorbed ether, heated to 107° C. liberated 10.2 grams of ether. Steam was then blown through it for 15 minutes, liberating 14.4 grams of additional ether with .755 gram of condensed steam. Further steaming gave no ether. There was considerable loss of ether due to insufficient cooling of the distillate.

Exp. II:

Steaming silica gel containing 33.8% acetone at 105° C. gave complete recovery of the acetone, using 1.63 grams of steam per gram of acetone.

Exp. III:

Steaming gel containing 21% benzene gave fairly complete recovery of the latter, using about 2.5 grams of steam per gram of benzene.

Air in Revaporization

The following plot from Miller shows the effect of air at varying velocities on the removal of water from silica gel. Curves 1, 2, 3, and 4 show the percentages of water removed for air rates of 5 to 50 cc. per minute per gram of gel. Curves 5 and 6 show the rate of air flow against time required to remove water at 120° C. and 105° C. respectively.

³ *Chem. Met. Eng.*, 23, 1219 (1920).

THE RECOVERY OF VAPORS

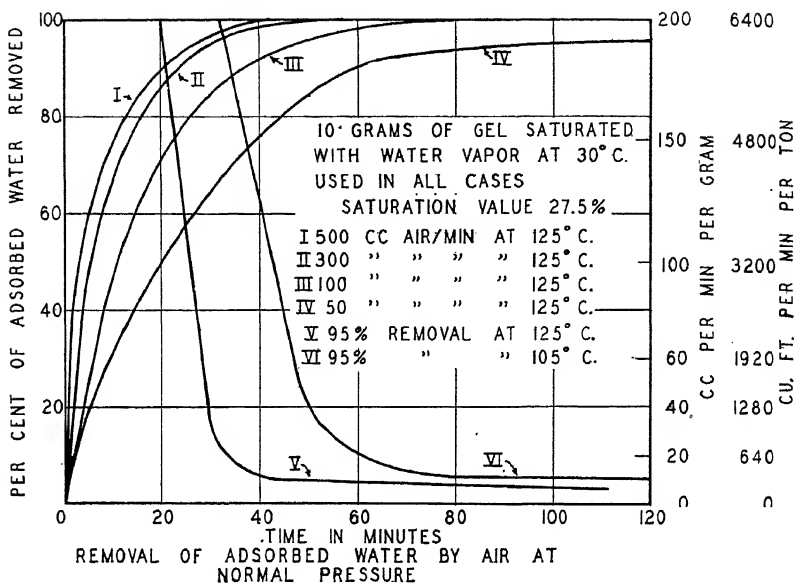


FIGURE 29.

Exp. IV:

Silica gel containing 15% and 24.7% of petroleum ether, when steamed at 107° C., required 15 grams of steam in 30 minutes to remove 85%, and 11 grams of steam in 10 minutes to remove 23 grams respectively.

Steaming Charcoal to Recover Gasoline

Tests by Burrell⁴ on the removal of adsorbed gasoline from charcoal indicate the following steam consumption in the recovery of the gasoline from the charcoal.

Heat Requirements.

Weight of gallon gasoline (lb.)	5.5
Saturation of 13 per cent by weight required, per lb. of charcoal	42.3
Specific heat of charcoal	0.3
Specific heat of gasoline	0.58
Latent heat of gasoline (B.t.u. per lb.)	100
Average b. p. of gasoline (° F.)	210
Highest temperature of distillation (° F.)	400
Temperature of charcoal by saturated steam (° F.)	230
Superheat (400°-230°) (° F.)	170

⁴ *Chem. Met. Eng.*, 24, 156 (1921).

Superheat required for charcoal ($42.3 \times 0.3 \times 170$)	2,157
Heat to raise charcoal 60° to 230° F.	170
Heat required to raise charcoal 60° to 230° F. ($42.3 \times 0.3 \times 170$)	2,157
Distillation of 60 per cent made without superheat.	
Heat required for gasoline distillation (60° to 230° plus latent heat) ($5.5 \times 150 \times 0.58$) (5.5×100) (B.t.u.)	1,030
Superheat required for 40 per cent distilled	411
Heat required for first 60 per cent distilled (B.t.u.)	618
Total heat required to raise to temperature of superheat (B.t.u.)	2,775
Total amount superheat required (B.t.u.)	2,568
Theoretical amount of heat required (B.t.u.)	5,343
Specific heat superheated steam 15 lb. 400° F.	0.5
Superheat available per lb. of steam $0.5 \times (400^\circ - 230^\circ)$ (B.t.u.)	85
$2568 \div 85$, lb. of water	30.21
Boiler feedwater ($^\circ$ F.)	200 $^\circ$
Boiler heat required (200° to 400° F.) (B.t.u. per lb.)	1,089
Total amount boiler heat required (30.21×1089) (B.t.u.)	32,900
Boiler hp. per gal. gasoline per day	0.045

These data have been found not to apply to modern commercial installations, perhaps because of vastly improved design and operating methods.

Chapter 12

Adsorption Apparatus for Solvent Recovery

Essential Parts of Recovery Apparatus

All types of apparatus for the recovery of solvents by adsorption consist of three primary parts: first, the adsorber, or container for the adsorbing medium; secondly, the source of supply of heated vapor or gas for revaporizing the solvent from the solid; and, thirdly, the condenser for recovering the revaporized solvent. The numerous modifications and accessories depend upon the materials used, local conditions, and the designing engineer.

Removal of Heat of Adsorption

There is one detail in solvent recovery work regarding which there may be required, for large-scale commercial operation, considerably greater attention than is the case with operation on a laboratory scale. The latent heat of condensation or adsorption of a condensing vapor must be removed as rapidly as it is liberated in order to prevent rise of temperature of the adsorbent. Little attention need be paid to this heat effect when the apparatus is small, since, owing to the fact that in small apparatus the ratio of outside surface (of a tank) to contents is relatively great, the heat evolved is readily lost by conduction and radiation from the surface of the container to the surroundings. On the other hand, in large-scale equipment, such heat effects may be serious, and when that is the case special provisions must be made to take care of them.

In actual practice as it is carried out in the United States at the present time, no special attention is ordinarily given to the removal of the heat of adsorption and no special equipment is used for this purpose. The reason for this is that practically all activated carbon recovery plants treat vapor-laden air or other gases where the concentration of vapor is very low. The heat of adsorption is therefore carried away to a large extent by the exhaust air system. In the operation of the Columbia Activated Carbon system, which will be described later, the carbon at the beginning of the adsorption period contains considerable water, and the vaporization of this water during the adsorption period prevents the heat of adsorption from causing undue rise of temperature in the adsorber.

Batch Operation

The simpler types of adsorption apparatus are intermittent in operation. For such apparatus, the relation between the capacity and the size of the adsorber can be expressed mathematically by the following differential equation:

$$(25) \quad u \frac{\partial y}{\partial x} + \alpha \frac{\partial y}{\partial \theta} + \beta \frac{\partial z}{\partial \theta} = 0$$

where y = concentration of vapor in the carrier gas, mols/mol
 z = concentration of vapor adsorbed on solid, mols/unit weight

u = carrier gas velocity in mols per unit time

α = mols of carrier gas per unit length of apparatus

β = weight of solid

x = length of apparatus

θ = time

This equation is based on a material balance where the solid adsorbent remains stationary while the gas passes through continuously. On account of the complicated relationship between y and z , however, there is no simple solution for the equation and for design purposes, and recourse is always had to small-scale, experimental data. It is important to remember, when

using such data for the design of larger equipment, that the heat flow relations will be entirely different as the size differs, and it becomes a problem in heat transfer to take care of the heat effect satisfactorily.

An example of the calculations involved in the design of a suitable adsorption apparatus is given in the following pages.

Example 17. It is desired to recover benzene from air by adsorption with activated carbon. There are to be handled 100,000 cubic feet of air per hour containing 0.5% by volume of benzene vapor as measured at temperature 70° F. and normal barometer.

$$\begin{aligned} & 78 \text{ (molecular weight of benzene, } C_6H_6) \times \frac{500}{359} \times \frac{492}{530} \\ & = 101 \text{ pounds of benzene to be condensed per hour.} \end{aligned}$$

The heat of adsorption of benzene at 70° F. is about 360 B.t.u. per pound.¹ The heat which must be removed per hour in the adsorber is therefore:

$$360 \times 101 = 36,000 \text{ B.t.u. (approx.) per hour.}$$

The weight of air per hour would be about:

$$\frac{99,500}{359} \times \frac{492}{530} \times 29 \text{ (mol. wt. of air)} = 7460 \text{ pounds per hour.}$$

Since its specific heat is about 0.24, the air would be heated in the adsorber, provided there were no other means of removing the heat evolved, to a temperature of about

$$70^\circ \text{ F.} + \frac{36,000}{0.24 \times 7460} = 90^\circ \text{ F.}$$

One of the most ingenious methods for keeping the solid adsorbent cool is of fairly recent invention. Formerly, when the solid was steamed in order to revaporize the adsorbed vapor, high-temperature, superheated steam was used for the purpose, as this left the solid dry and highly reactive. It has been found, however, that if the solid is left wet with water after the steaming, and if the vapor to be adsorbed will displace the water during the adsorption process, the heat evolved

¹ For heats of adsorption see Lamb and Coolidge, *J. Am. Chem. Soc.*, 42, 1164 (1920).

by the condensing vapor will supply the heat needed for the vaporizing water so that there will be none left for raising the temperature of the solid until most of the water is gone. By skillful operation, therefore, it is possible to run a batch adsorption process without the necessity of having either internal or interstage coolers.

In this particular example, on account of the very moderate rise in temperature of the air indicated, no special provision need be made for removing the heat other than making sure that the activated carbon contains enough water at the start of operations to take care of the bulk of it, which in this case would be the equivalent of vaporizing about 40 pounds of water per hour.

Usually, however, the vapor-laden air comes to the adsorber hot from the previous vaporizing operation and must be cooled down to a suitable adsorption temperature by some sort of cooler.

Air coolers may be either direct or indirect, that is, the air may be cooled by direct contact with the cooling medium, such as a water spray, or it may be cooled by contact with cooling surfaces which are kept cool by some medium such as water on the other side of the surface, as in the case of tubular condensers. The former, or direct cooling, is always less expensive if the nature of the gases and vapors handled will permit its use. It is suitable where the gas or vapor is not appreciably soluble in the cooling medium. For instance, in this case benzene is not appreciably soluble in water. Therefore the air containing the benzene vapor may be passed through a water spray which would cool it to the desired temperature without dissolving the benzene. On the other hand, if the vapor in the air were alcohol, which is soluble in water, indirect cooling would be necessary.

For direct cooling with spray chambers of standard design, the size of chambers required may be figured approximately from the following equation:

$$(26) \quad \frac{Q}{\theta} = (ha) V (\Delta t)_{\text{average}}$$

where $\frac{Q}{\theta}$ represents the heat to be removed from the air per unit time, (ha) is the coefficient of cooling in multi-stage spray coolers (where the air remains substantially saturated with water after the first stage, it will have a value under these conditions of about 30 B.t.u. per cubic foot of spray chamber volume per hour per degree Fahrenheit difference between water and air temperature), V is the volume of the spray chamber, and (Δt) the average difference in temperature between the water and the air.

Suppose that the benzene-laden air comes to the adsorber at 200° F. and that it must be cooled to 70° F. before entering the adsorption chamber. The heat that must be removed per hour will be approximately, neglecting the presence of the benzene,

$$\frac{Q}{\theta} = 7460 \times 0.24 \times (200 - 70) = 230,000 \text{ B.t.u.,}$$

the average air temperature will be $\frac{200 + 70}{2} = 135^\circ$ and if the water spray temperature rises from 50° F. to 60° F., its average temperature will be 55° F.

$(\Delta t)_{\text{average}}$ will therefore be $135 - 55 = 80^\circ$.

Inserting these values in equation 26 gives the required volume of the spray chamber to be

$$V = \frac{230,000}{30 \times 80} = 96 \text{ cubic feet.}$$

Air washers of this type have one or more banks of atomizing spray nozzles, the air being blown by means of a fan through the spray, usually in the direction of the spray. The air then passes through a set of plates forming a zigzag passage for the purpose of removing the water entrained by the air. The water may be recirculated through the sprays, being cooled or heated as the case may be, the loss of water by evaporation being made up from some external source.

For indirect cooling, the amount of cooling surface depends almost entirely on the velocity of the air by the surface. An approximate equation for air flowing through small pipes is as follows:

$$(27) \quad \frac{Q}{\theta} = 2.4 \times V^{0.8} \times A \times (\Delta t)$$

where V is the pounds of air flowing per square foot of cross-section of the pipe per second, $\frac{Q}{\theta}$ is the heat transferred in B.t.u. per hour, and A is the area of cooling surface in square feet. (Note: For reasonable air velocities, the resistance to flow of heat of the dividing walls if of metal, and of the liquid film on the cooling water side, may be neglected.) Thus if the 7460 pounds of air in question are to be cooled by flowing through a tubular cooler consisting of 100 2-inch inside diameter tubes in parallel, the amount of cooling per foot of length of the tube would be calculated as follows:

Area of cross-section of 2" tube = 3.14 sq. in. = .0218 sq. ft.
100 tubes would have $100 \times .0218 = 2.18$ sq. ft. total cross-sectional area.

$$\text{Therefore } V = \frac{7460}{2.18 \times 3600} = 0.95 \text{ lb. per sq. ft. per sec.}$$

The surface of a 2" tube 1 ft. long is

$$\frac{12 \times 2 \times 3.14}{144} = 0.52 \text{ sq. ft.}$$

The surface of the 100 tubes would therefore be 52 sq. ft. per foot of length.

If the water and air be at the same temperatures as before, therefore $\Delta t = 80^\circ$ and

$$\frac{Q}{\theta} = 2.4 \times (.95)^{0.8} \times 52 \times 80 = 9600 \text{ B.t.u.}$$

per hour per foot of length of the tubes.

Since there are 230,000 B.t.u. to be removed per hour, the cooler must have tubes $\frac{230,000}{9600} =$ approximately 23 feet long.

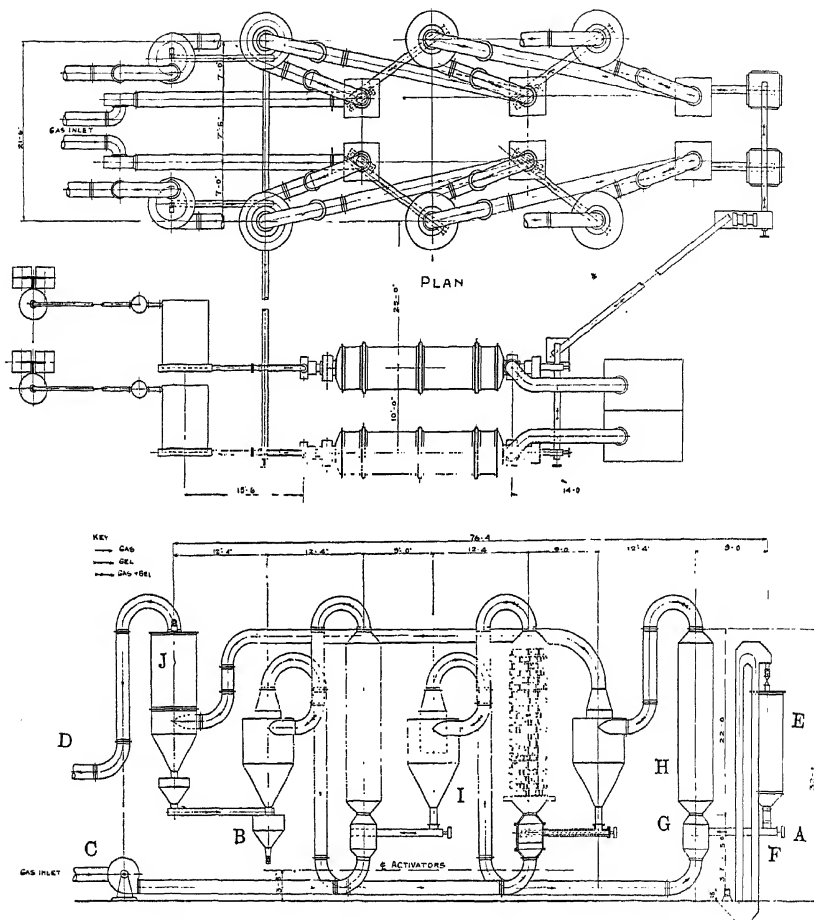


FIGURE 30. Silica Gel Adsorption Plant, Plan and Elevation.

This represents a three step counter-current adsorption plant, the gel powder entering at the right at A and leaving at B, while the gas containing the solvent enters at C, and leaves at D. The operation of the system is as follows: The gel is raised by means of an elevator and discharged into the supply tank E from which it is delivered continuously by the screw conveyor F to the chamber H where it meets the nearly dissolved air coming from the previous step. The mixture of gas and gel then passes up through the cooler H (Figure 32) of radiator-like sections through which cooling water is passing. The mixture is then discharged to the cyclone dust collector I, where the bulk of the gel is separated from the gas, the gel being delivered to the previous step, while the exhausted gas goes to a final bag filter J to remove the last of the gel, before leaving the system. The saturated gel is delivered from the hopper B to an activator which is illustrated in Figure 31.

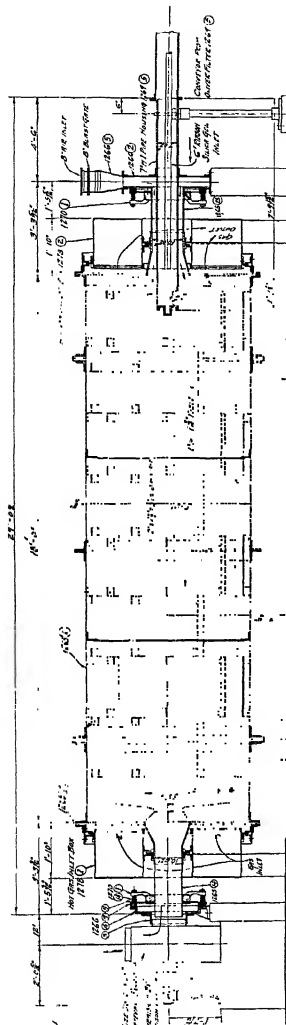


FIGURE 31. Silica Gel Activator.

A rotary cylindrical shell through which the gel is passed from right to left, in contact with longitudinal flues heated by hot gases. The gel and liberated solvent are discharged axially from the left hand end to condensers and dust collectors.

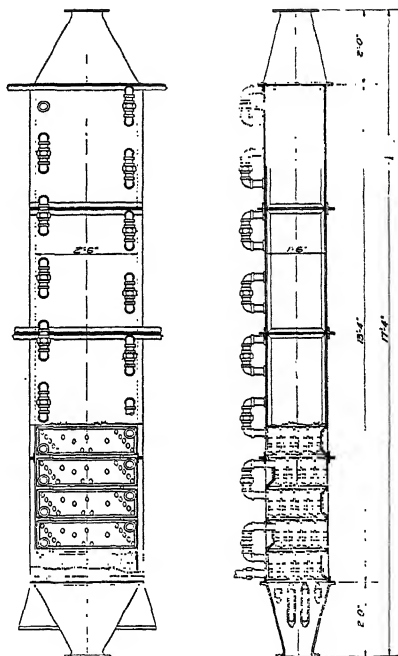


FIGURE 32. Silica Gel Cooler.

Design of Coolers

It should be appreciated that the design of a cooler, or of any apparatus, for that matter, should involve an economic balance between the cost of the cooler and the cost of operating it. In such a case, the cooler may be made smaller with higher air velocity, and do the same amount of work; but the cost of forcing the air through it, with the increased friction due to the higher velocity, may more than offset the saving in cooler cost. As a general rule standard equipment will be found most suitable on this account, as it has run the gauntlet of costs, and is probably the least expensive in the end.²

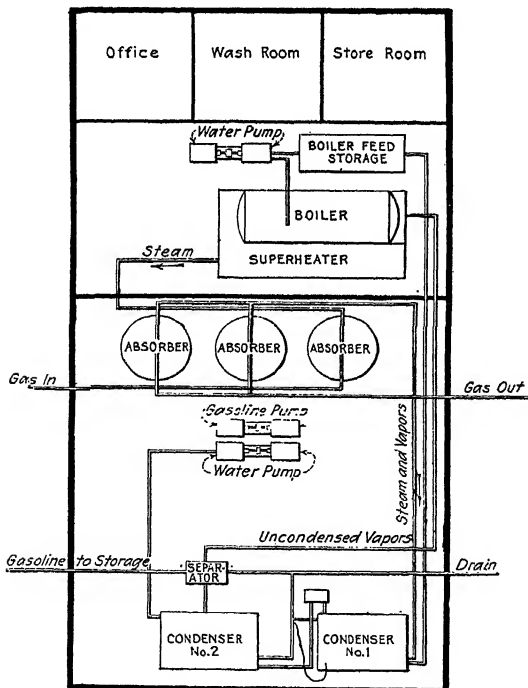


FIGURE 33. Early Gasoline Adsorption Plant.

²For further information on coolers, see Walker, Lewis, McAdams and Gilliland, "Principles of Chemical Engineering," 3rd edition, 1937.

Burrell Adsorption Plant

The original apparatus used by Burrell³ for the extraction of gasoline from natural gas by adsorption on activated charcoal is shown in Figures 33 and 34.

The adsorbers were filled with coconut shell charcoal of from 8 to 14 mesh, which when packed to a depth of 5 feet is said to offer from 1 to 2 pounds per square inch pressure resistance to flow of gas when the

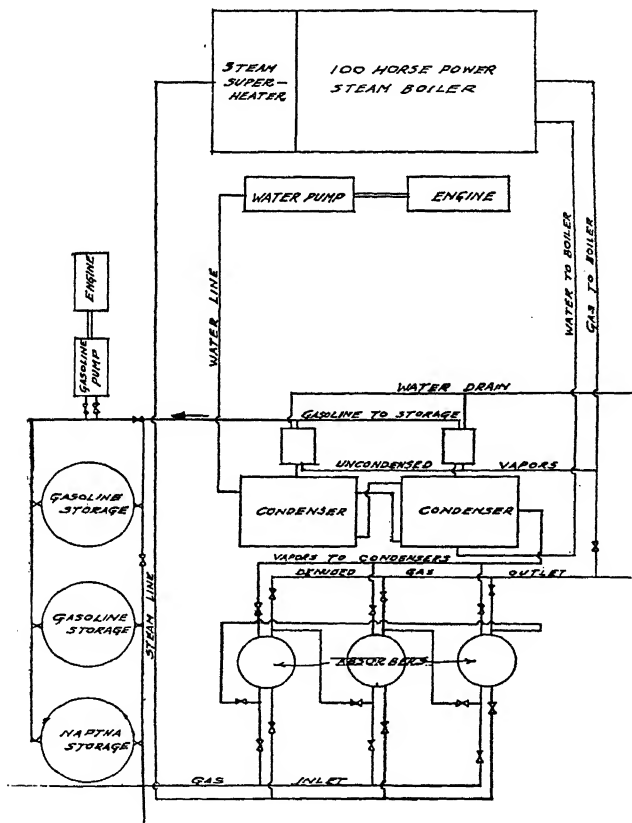


FIGURE 34. Early Gasoline Adsorption Plant.

³ Chem. Met. Eng., 24, 156 (1921).

gas is passing through at the rate of 40 cubic feet per hour per square inch of cross-sectional area.

In that particular case, temperature rise was not serious, since the gases are dilute, and the heat evolved served principally to drive out of the charcoal the more volatile portions of the gasoline which it is not desired to collect. A temperature rise of 60° has been observed.

The use of three adsorbers permitted one to be cut out of the system when saturated, for gasoline removal and reactivation, while the other two are operating in series. The gasoline was recovered by passing steam through the charcoal, and condensing the mixed steam and gasoline in the condensers as shown. The table on page 88 indicates the heat consumption reported for this process.

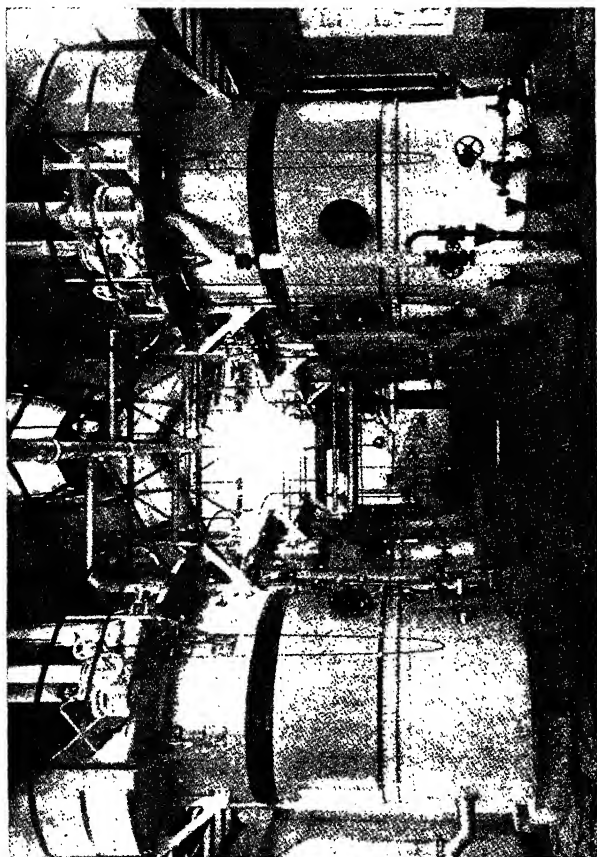
The Recovery of Natural Gasoline from Natural Gas*

Early experiments in the extraction of gasoline from natural or "casinghead" gas were carried out in the United States as early as 1918. The work of Burrell and his collaborators, to which passing reference has been made above, deserves particular credit as a pioneer endeavor toward the development of a new industry. It is true that those early extraction plants, designed and installed without any background of experience and very little experimental data of practical use, were far from efficient on the basis of present-day standards; but they provided the impetus which led to the commercial development of activated carbon systems for industrial adsorption of gases and vapors.

Not only were the early plants installed in the United States, but the first foreign installation was of American design. In recent years the activated carbon process has almost disappeared from the American scene insofar as the extraction of gasoline from natural gas is concerned, while at the same time it has flourished in foreign lands and reached an extremely high standard of efficiency.

* E. L. Luaces, Dayton, Ohio.

FIGURE 35.
Standard Gasoline Re-
covery Plant Having a
Daily Capacity of 20
Tons.



Modern practice makes use of from four to eight adsorbers. Usually the initial installation consists of four adsorbers, and more are added in groups of two. There is one plant where the number has reached a total of twelve. The operating scheme provides for two adsorbers in the adsorption cycle, one steaming, and one drying and cooling. The cycles of adsorption are so arranged that the end-points of the two adsorbers come a half-hour apart. If a new plant is started and the cycle of adsorption is to be 90 minutes, then two adsorbers are placed in parallel service but the first one is cut out at the end of 45 minutes (when only half full). A third adsorber is then cut in, and at the end of the first 90 minutes of operation this third adsorber will be half full while the second will be full. Then the second is cut out and the fourth cut in. In that way the greatest of flexibility is attained. The gas enters the carbon at a maximum temperature of 33° C. Multiple-bed adsorbers are used, the gas flow being in parallel through the several beds. This calls for elaborate internal construction. The adsorbers are provided with built-in heat regenerators. Gas flow is upward and steaming downward. The temperature of the steam is seldom higher than 270° F. throughout the entire cycle. The steam passing downward through the carbon vaporizes the gasoline, and the mixture of steam and gasoline vapors passes through the heat regenerator on the way out of the adsorber. The regenerator picks up part of the heat load. When the steaming has been completed, either air, or more safely and conveniently, denuded gas, is passed upward through the adsorber for drying and cooling the carbon. In passing through the regenerator, the drying and cooling fluid will pick up heat from it, and in passing through the carbon beds will give up this heat in the evaporation of the moisture in the carbon. The regenerating mass (generally a bed of small stones) and adsorbent mass are so proportioned that by the time the heat has been removed

from the regenerator the carbon will be dry. Then it is only necessary to continue the flow of drying and cooling fluid through the adsorber to cool it down to substantially room temperature.

More recently the matter of selective adsorption has come up again for attention, and the work done so far indicates that success is to be realized. In substance, the scheme provides for double adsorption of the gas: first with an adsorbent of comparatively large pores and low activity, and secondly with the usual type of adsorbent and in the usual manner. In practice, the first set of adsorbers is utilized for the recovery of products which are liquid at ordinary temperature and pressure, and the second set for the recovery of products which are not liquefiable at ordinary temperature and pressure. The only products permitted to pass through are methane and ethane, which are then used as sources of heat or are transformed catalytically or otherwise into synthetic gasoline or other products. The second set of adsorbers removes products such as butane and pentane, which are polymerized. It was formerly believed that one of the few disadvantages of the carbon process was that it had to have much attention for the setting of the valves. This disadvantage does not exist because the entire process may be carried out completely automatically on a predetermined cycle by proper application of suitable instruments. In the double adsorption system, the first set of adsorbers generally handles gas at from 7 to 12 atmospheres, while the second set of adsorbers handles gas at from 6 to 8 atmospheres pressure.

Wilson and Lamb's Suggested Plant

In an attempt to devise a continuous system, Wilson and Lamb proposed to use ferric hydroxide gel, $\text{Fe}(\text{OH})_3 \cdot n \text{H}_2\text{O}$, as a solid adsorbing agent in a suitable apparatus to give continuous counter-current contact between the solid and gas. Such an apparatus

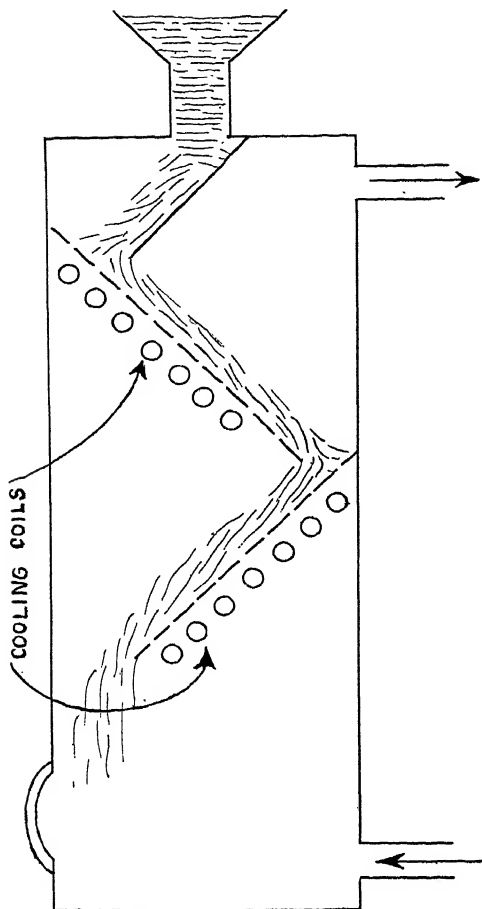


FIGURE 36.

Wilson and Lamb's
Suggestion for an Ad-
sorption Tower.

might be constructed as shown in Figure 36. It would be suitable only for hard non-friable solids, as easily pulverized solids, such as carbon, would not be especially satisfactory on account of the dust produced.

Another device, Figure 37, designed to give counter-current contact between the adsorbing medium and other solid material containing solvent which is to be removed, is described by Wilson as follows:

A perforated belt is repassing through a chamber through which is rising a current of gas. Solid material containing the solvent to be vaporized falls from a hopper, *B*, onto the belt where it travels slowly to the point *D*. Here it is removed from the belt and discharged from the apparatus. The adsorbing agent enters from a similar hopper, *A*, onto that portion of the belt immediately above, and travels counter-current to the solid from *B*. The gas picks up solvent, being cooled in the process, and when coming into contact with the adsorbent above, gives it up again, being

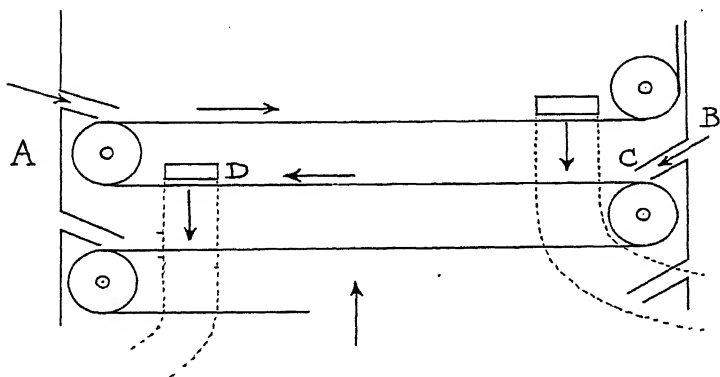


FIGURE 37. Wilson's Adsorption Apparatus.

reheated at the same time, by the heat of adsorption. So far as is known, no such machine has ever been built.

The recent adoption of solid adsorbents in solvent recovery accounts for the large amount of descriptive matter available at the present time. In general, it may be stated that the field of solid adsorbents lies in the handling of dilute rather than concentrated gases.

Suitability of Adsorbing Agents

So far as individual adsorbing agents are concerned, carbon has the greatest capacity, but is not suitable for high temperatures, or for gases containing oxygen or

other oxidizing agents. Silica gel, activated alumina, and ferric hydroxide gel are chemically inert, the two former especially so. These three gels are particularly suitable for the removal of water vapor from air for drying or air-conditioning purposes, and are not generally used for solvents.

Activated alumina is one of the more recent adsorbing agents. It is particularly suitable for the removal of water vapor from air and other permanent gases,

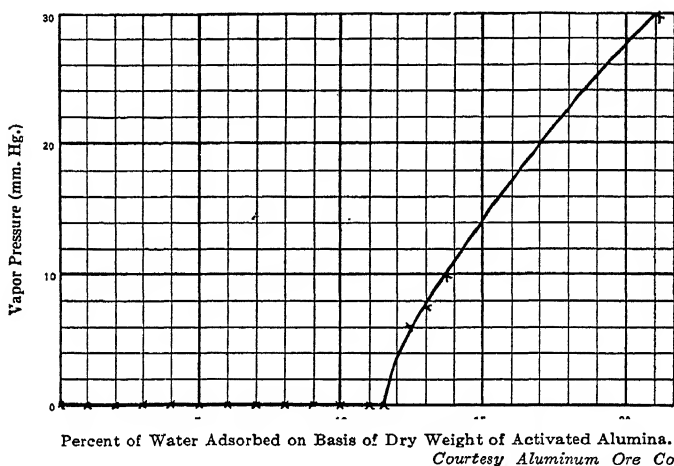
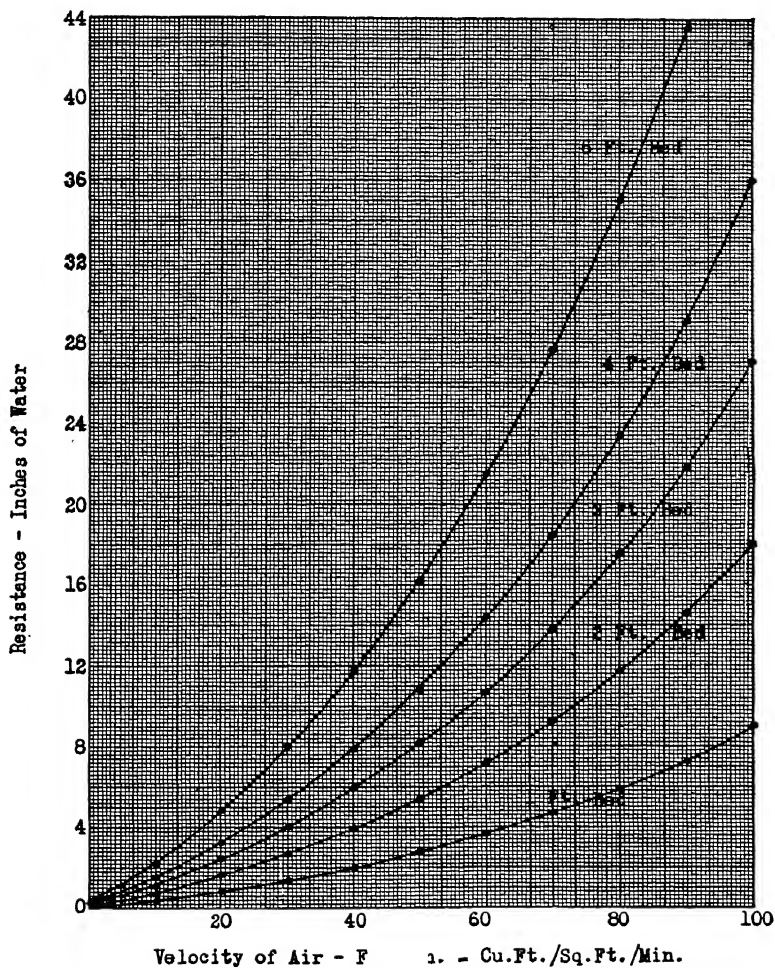


FIGURE 38. Variation of Vapor Pressure with Percentage Adsorption from Air at 30° C. and 90% Relative Humidity for 8-14 mesh Activated Alumina by the Dynamic Method.

adsorbing it preferentially with respect to other vapors present. Figure 38 from the Aluminum Ore Company, shows the equilibrium partial pressure of water vapor over 8-14 mesh activated alumina at 30° C., in contact with air at approximately normal barometer. It would appear from this diagram that the larger portion of the adsorption is due to the monomolecular layer and that the rest is similar to the case of silica gel, that is, the absorption probably is due to capillary openings on the surface of the gel.



Courtesy Aluminum Ore Co.

FIGURE 39. Resistance to Flow of Air by 8-14 mesh Activated Alumina.

For the removal of water vapor from air, it is recommended that the temperature be kept below 90° F. and that a rate of flow of from 10 to 20 cubic feet of gas per hour per pound of activated alumina be used. The chart in Figure 39 shows the pressure drop of air

expressed in inches of water due to flow through beds of several depths of 8-14 mesh activated alumina plotted against the air velocity.

In general, a tower height equal to 3 or 4 times the diameter has been found to work well for a variety of adsorbents. Reactivation is done by means of hot gases or direct heat.

Recovery of Light Oil from Coal Gas by Use of Activated Carbon

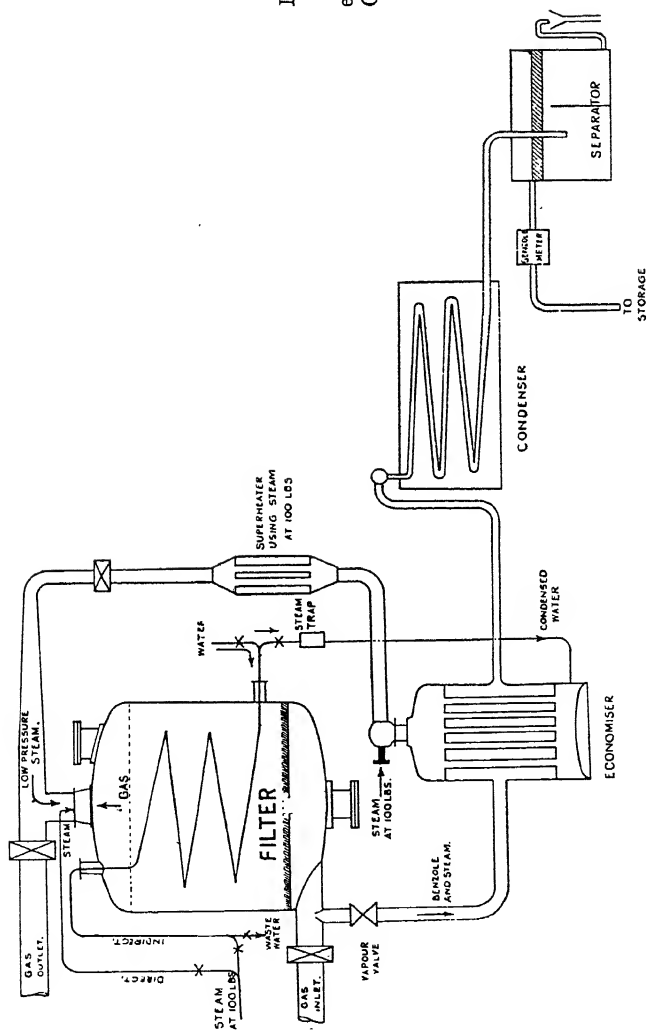
Light oil, which is a mixture of benzene, toluene, the xylenes and other substances, was formerly always recovered from coal gas by washing the gas with a heavy petroleum oil in which these substances are soluble. The success attending the recovery of other vapors from gases by adsorption has led in recent years to the use also of activated carbon for the recovery of light oil.

It is known that at least one commercial installation recovering light oil from coal gas with zinc chloride-activated carbon was in operation in Germany prior to the first World War.

Figure 40 represents one of the smaller plants installed in England to handle 2,000,000 cubic feet of gas per day. It consists of four filters in parallel, each one being 6 feet in diameter and 5 feet high, and containing approximately 2,000 pounds of activated carbon per filter. The diagram shows one of the filters with the accessory equipment, while the four filters are shown in Figure 41.

The coal gas, freed from naphthalene by a previous washing with oil, is passed through any two in parallel, entering at the bottom, passing up through the filter, and leaving at the top to the left. When the break-point for the benzene in the exit gas is reached, the flow is shifted to another filter, and steam at 100 pounds per square inch gauge pressure is admitted to the coil in the filter. After about one hour, when the temperature

FIGURE 40.
Benzol Recovery Plant, Active
Carbon Process.



of the carbon has reached 100° C. at the top of the carbon, open steam is admitted to the top of the filter and flows down through the charcoal, steam distilling the adsorbed vapors out through the bottom. The open steam is at low pressure, but has been superheated by means of the 100 pound steam as shown in the diagram. It is produced by revaporizing some of the condensed

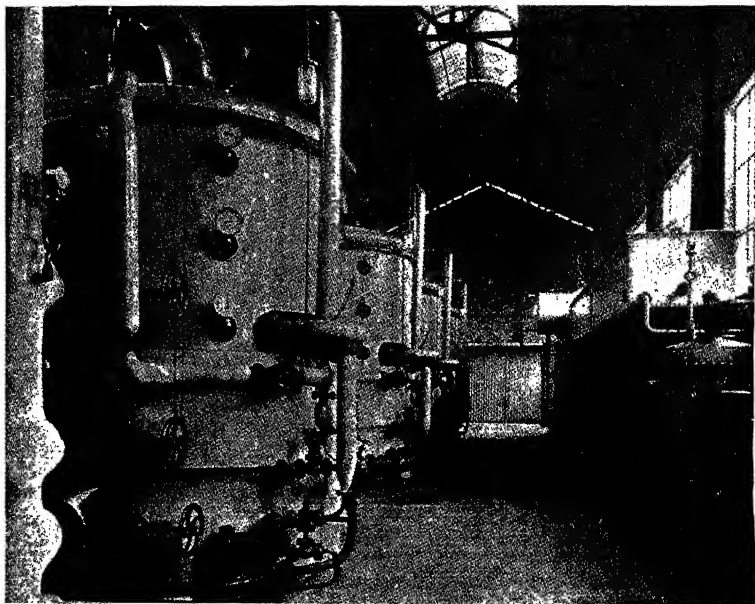


FIGURE 41. Benzol Recovery Plant.

steam from the coil in the economizer and mixing it with fresh high-pressure steam in an injector. The light oil-steam mixture flows to a condenser and then to a gravity separator. Open steam is allowed to flow until no more light oil appears at the separator. This requires approximately one hour. Cooling water then replaces the steam in the coil to cool the carbon for the next cycle, the cooling process requiring about 30 minutes.

In any one cycle, the carbon picks up the adsorbable vapors in layers according to their relative adsorbability. In order, these are naphthalene, xylene, benzene, unsaturated hydrocarbons, carbon disulphide, hydrocyanic acid, sulphides, and finally the more permanent gases. At the end of the adsorption period, any naphthalene will be found in the bottom layer with the other less volatile substances in order above it. By blowing the open steam through the carbon in the opposite direction to the flow of the original gas, the naphthalene, together with any tarry matter which might accompany it, goes out without coming into contact with the rest of the carbon and plugging it up.

The carbon loses its adsorbing power gradually, and finally must be replaced—in favorable cases after 600 to 900 cycles. It appears that the presence of hydrocarbon vapors and hydrocyanic acid in the carbon for any length of time while it is hot causes more rapid deterioration of the carbon. Under favorable conditions, 150 pounds of light oil may be recovered per pound of carbon consumed, while the steam and water consumption per pound of light oil produced may amount to 3 pounds and 70 pounds respectively. The light-oil yield per cycle at the point when the carbon is discarded drops to about 20 per cent of the production with fresh carbon.

Recovery of Rubber Solvents

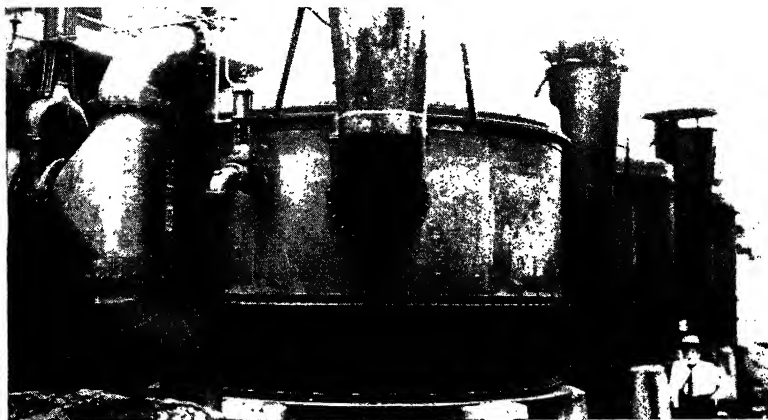
The rubber industry has been one of the most prominent users of solvent recovery, both by means of carbon adsorption and by the older methods to be described later. While the choice of rubber solvents varies with circumstances, for purposes of this discussion, only two of the common ones will be mentioned, namely, benzol or commercial benzene, and gasoline or special cuts of petroleum. The former of these two solvents, while an excellent solvent for rubber, suffers the severe handicap of being somewhat poisonous, and

several states have passed legislation prohibiting its use for many purposes.

Usually, the rubber mixture to be used is dissolved in the solvent in question to form a plastic mass which may be applied to the textile fabric or other base. The rubberized fabric is then heated to evaporate the solvent and subsequently vulcanized or otherwise finished. The solvent used is very volatile at room temperature, and if not entirely enclosed, vapor readily escapes into the room. If the vapor reaches a concentration of 1.5% by volume in the air of the room, the resulting air-vapor mixture is violently explosive. If the vapor in question is that of benzene, the mixture is poisonous as well as explosive.

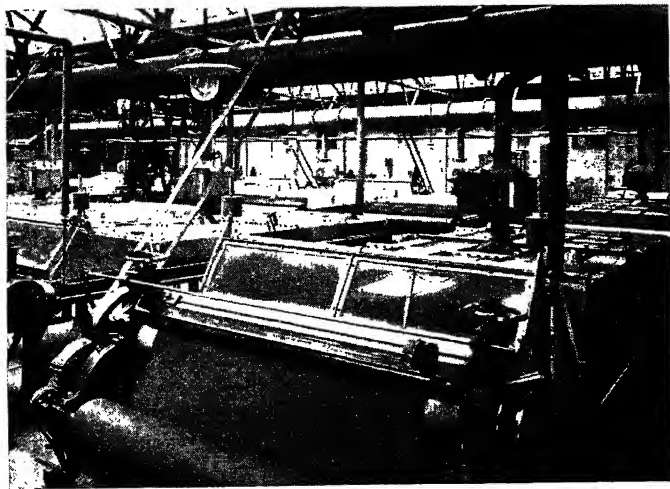
Therefore, in order to keep the concentration of the solvent vapor in the air well below the lower explosive limit, it is customary to ventilate the rooms in which the solvent is vaporized by drawing through them large volumes of air. This practice results in a very dilute solvent-air mixture, consequently making the recovery of any considerable proportion of the solvent a very costly procedure. The only feasible method of such recovery is by adsorption, a method sometimes resorted to even with extreme dilutions of solvent in air.

When solvent recovery is undertaken, it becomes necessary to enclose the apparatus where the vaporization is taking place in order to raise the solvent concentration to a point not too far below the lower explosive limit in order to lessen the cost of recovery. The safe limit is about 1 per cent by volume, and if it is carried as high as this figure, great care must be taken that no pockets are present where gas of higher concentration may collect. Some factories prefer to keep the concentration below 0.5% by volume as a matter of safety. Enclosure must be begun at the mixers where the solvent is added to the rubber compound. Also, the spreaders or sheeters where the solvent is applied to the fabric and subsequently vaporized must be enclosed.



Courtesy E. L. Luaces and Associates

FIGURE 41a. Three double-bed adsorbers recovering 1500 pounds of mixed solvents per hour in an artificial leather and shade-cloth plant.



Courtesy Acticarbone Corp.

FIGURE 41b. Collection of vapors from horizontal spreading machines in English artificial leather plant.

The enclosures are furnished with ample windows so that the workmen can see what is taking place and can get at the fabric readily. A point of greatest importance is to see that all places where static electricity might collect are thoroughly grounded. Also, all pipes through which the solvent-air mixture flows should be supplied with flame arresters in order to localize any fire which might occur in them.

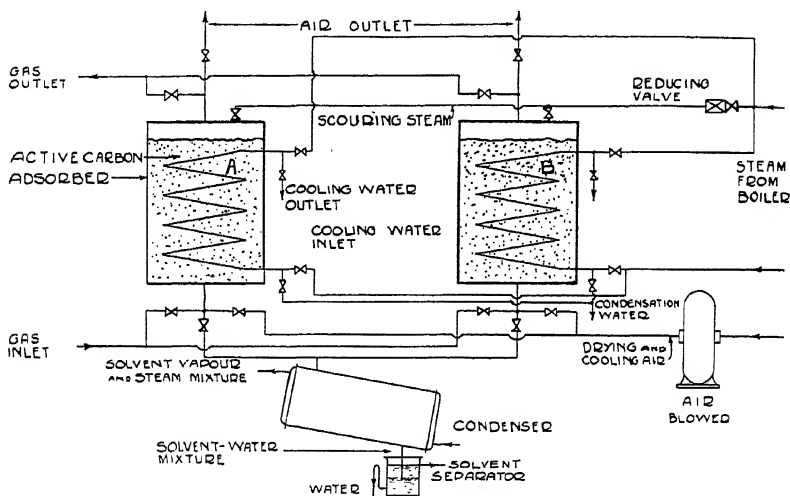


FIGURE 42. Diagram of Principal Parts of a Recovery Plant (Steam Method).

A common type of recovery equipment is shown in the diagram in Figure 42.

In this apparatus, the gas from the spreaders enters the adsorbing tower at the bottom and is discarded from the top. When the break-point is reached, the tower is cut out and the other one cut in. During the adsorption, the heat developed may be partially removed by running cold water through the cooling coil in the carbon, or by mixing cool, solvent-free air with the incoming gas. After the tower is cut out, steam (instead of cold water) is turned into the coil, and the

carbon heated. Open steam is then introduced at the top of the tower and the steam plus the vaporized solvent flows from the bottom into a condenser and separator. The carbon is then cooled and dried by blowing cold, fresh air through it, after which it is ready for reuse.

Data from plants using this process indicate that when the solvent content of the entering air lies between 15 and 25 grams per cubic meter, that is, between 0.4 and 0.7 per cent by volume, the recovery may run between 85 and 90 per cent of the solvent used. Under similar conditions, it appears economical to operate an adsorption plant for these relatively inexpensive solvents when the solvent content of the entering air is as low as 0.1 per cent by volume. It is necessary, in order to get this high recovery, to be sure to enclose, with hoods leading to the main suction lines, the mixers where the rubber compound is dissolved with the solvent. The carbon consumption depends on variable factors, including cleanliness of the air entering the apparatus, the amount of wetting of the carbon, the temperature to which it is heated in the revaporization process, and so forth. Data seem to indicate that under favorable conditions, the loss may amount to as little as 0.05 to 0.10 per cent of the solvent recovered.

Recovery of Alcohol From Fermentation Gases*

In the fermentation of sugars to form alcohol, approximately one-half of the sugars are transformed into alcohol and the balance into carbon dioxide. The gas is given off at a non-uniform rate and the temperature of fermentation varies. Depending upon the stage of fermentation and the temperature, from 0.75% to 1% of alcohol vapors is carried off with the gas. The Backus process[†] for the recovery of this alcohol provides for the removal of the alcohol vapors by scrubbing

* E. L. Luaces, Dayton, Ohio.

† U. S. Patents 1,493,183; 1,510,373.

the gas with water which is then used for diluting the molasses to be fermented, the scrubbed gas being then deodorized by passing it through activated carbon.

In the Acticarbhone process the removal of the alcohol vapors is accomplished by adsorbing them on carbon. The system generally consists of four adsorbers, two of which are alternately used for alcohol recovery and two for deodorizing. The gas from the fermenters is put through a separator to remove entrained water and is then admitted to the alcohol recovery unit. When the adsorber is saturated with alcohol vapors, the flow of gas is diverted to a second adsorber and the first is steamed to remove the adsorbed alcohol. The distillate is condensed giving a solution of from 10 to 12% alcohol which is subsequently rectified. After steaming, the adsorber is dried with warm air and cooled to at least 90° F. for reuse.

The deodorizing unit takes the de-alcoholized gas and removes odors from it. Since the major proportion of odorous impurities has been taken out in the recovery unit, the cycles of adsorption are much longer in the deodorizing unit, which is generally much smaller in size. Great care must be exercised in designing the deodorizing unit, in view of the fact that the removal of the last trace of impurities is a delicate and necessary thing in order to produce a gas suitable for the manufacture of Dry Ice (solid carbon dioxide).

The value of the alcohol recovered is generally sufficient to cover the cost of the recovery, the entire system being operated automatically.

Recovery of Carbon Disulphide in Viscose Rayon Production*

In the manufacture of viscose products raw cellulose material is treated with caustic soda to produce "alkali cellulose." After aging, the alkali cellulose is treated with carbon disulphide to form "cellulose xan-

* E. L. Luaces, Dayton, Ohio.

thate." During this reaction, heat is generated and carbon disulphide is driven off. When the reaction has been completed, the xanthate is dissolved in weak caustic solution and the resulting viscous mass or "viscose" is stored at low temperature to mature. When the proper degree of ripeness has been attained, the viscose solution is forced or extruded through fine orifices into an acid coagulating bath and filaments in the form of rayon fibers are formed. The viscose solution also may be cast in suitable molds to form articles of various shapes, or extruded through thin slits to form sheets. Coagulation of the viscose solution decomposes it with the formation of regenerated cellulose; hydrogen sulphide, carbon disulphide and other compounds are liberated.

Methods hitherto used for the recovery of carbon disulphide vapors driven off in the production of viscose products have not been fully successful. Recent developments in the United States have emphasized the desirability of recovering this material on account of its toxic nature. The concentration of these vapors in the air collected around the points of evaporation is extremely low and recovery methods based upon direct condensation or on refrigeration cannot successfully be applied. Liquid absorption methods likewise suffer because of the low concentration of vapors in the laden air. Adsorption on solid adsorbents is also difficult due to the fact that the hydrogen sulphide present in the vapors collected materially reduces the effectiveness of the adsorbent with the result that it quickly becomes spent and must be replaced. The Sorbit process* provides for the removal of hydrogen sulphide and other impurities from the laden air by washing with a suitable liquid and by subsequent recovery of the carbon disulphide vapors with a solid adsorbent.

In practice, the vapors given off from the various parts of the process are collected mixed with large vol-

* Patents pending.

umes of air. The laden air is passed through a scrubbing tower through which is circulated the liquid absorbent which dissolves hydrogen sulphide and other impurities from the air but permits the carbon disulphide vapors to pass through. The washed air is then passed through adsorbers provided with a bed or beds of a suitable adsorbent carbon, and the denuded or stripped air is permitted to pass out from the upper portion of the adsorber. Three adsorbers are used, but only one is in the adsorption cycle at any given time.

When the adsorbent carbon bed or beds in the adsorber have reached practical saturation, the flow of laden air is diverted to a second adsorber and the first is regenerated by passing steam through it in a downward direction. The steam drives out the adsorbed carbon disulphide which is then condensed and separated by decantation.

The adsorbers are equipped with heat regenerators in their lower sections. These regenerators adsorb part of the heat load of the steam-CS₂ mixture passed through them during steaming, and are warm at the completion of this operation. The beds must be dried and cooled to condition them for further use. Room air is passed upward through the adsorber, first passing through the heat regenerator in the lower section of the adsorber and then through the carbon bed or beds in the upper section of the adsorber. In so doing, the air picks up heat from the heat regenerator and gives it up to the carbon, thereby driving out moisture held by the carbon from the steaming operation. This is continued until the regenerator has given up all the heat retained by it, when the carbon will have been dried out. The cooling cycle follows by continuing the passage of room air through the adsorber.

When three adsorbers are used, one is in adsorption, one being steamed, and one dried and cooled. This makes it possible to have a continuous stream of warm water flowing from the condenser in which the steam-

CS_2 mixture is condensed, and this water is used for washing freshly coagulated viscose products. The temperature is controlled so that it will be above the boiling point of carbon disulphide, and preferably between $65\text{--}70^\circ\text{C}$. Any excess water is circulated through a cooling tower and returned to the process together with makeup water.

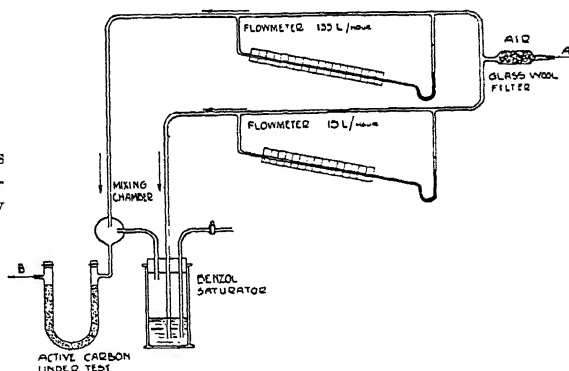
It appears possible to recover carbon disulphide in viscose plants when the concentration is as low as 5 grains per cubic foot.

Determination of the Activity of Activated Charcoal

The method given by E. Reisemann for determining the adsorbing power of activated carbon is substantially a laboratory run along the same lines as the plant operation. The apparatus is shown in Figure 43.

FIGURE 43.

Urbain Process
to Measure Ad-
sorption Activity
of Carbon.



Clean, filtered air enters at A and is divided into two streams, each passing through a flow meter to determine its rate. One of these streams then passes through a saturator where it is saturated with benzene vapor and is then mixed with the other stream so that the resulting gas contains 30 grams of benzene per cubic meter. This gas then flows through a U-tube containing a weighed amount of the carbon to be tested. The

flow continues until the carbon shows no further increase in weight. This procedure thus measures the adsorbing power of this particular sample of carbon, when in equilibrium with a particular mixture of vapor-air, at a certain temperature. Vapor of the same solvent as that to be recovered in the plant should be used in making the Reisemann test.

The determination of the break-point of the carbon may be made in the same apparatus at the same time, by attaching another U-tube containing carbon, beyond the tube previously mentioned, and determining by means of a gas meter attached to the line, the amount of air which has passed through when the second U-tube first shows the slightest increase in weight.

This same test will give a measure of the solvent content of the air, since when the break-point of the first tube is reached, all the solvent in the air up to that instant has been caught by the first tube, and the increase in weight of that tube up to that time divided by the volume of air which has passed through the apparatus, will be the average solvent content of the air during that period. This calculation will enable one to determine if the air used had the proper solvent concentration for the test, and if used without the preliminary saturator, on the gas which is to be treated by the plant equipment, it will give the solvent content of that gas.

Chapter 13

Commercial Activated Carbon Systems

In previous chapters it has been pointed out that the outstanding feature of solvent vapor recovery has been the very great growth during the past two decades of the use of activated carbon for this purpose.

Several grades and types of activated carbon are commercially available for the recovery of solvent vapors and for other uses. Those used for solvent recovery are in the form of hard, strong granules or pellets ranging in size from about 1/4 inch to 1/16 inch, and weighing from 25 to 34 pounds per cubic foot. These carbons are usually manufactured from coconut shells, although certain other materials may be used. During the manufacturing process, the carbonized coconut shells or other materials are subjected to a controlled gaseous oxidation treatment, or chemical attack at a high temperature, which removes impurities and increases porosity without reducing strength or hardness.

The development of this system of solvent recovery has made it possible to recover efficiently, profitably and safely almost any quantity of solvent under conditions which permit the vapor-laden air to be collected from the manufacturing operation, even though the vapor concentration is extremely low and water vapor is present. The plants vary widely in capacity. Some small plants recover less than ten gallons of solvent per day, whereas large plants recover over 25,000 gallons per day.

To recover the solvent vaporized in a manufacturing operation, the mixture of solvent vapor and air, or other gas, is usually collected by a hood or enclosure

which is maintained under a slight negative pressure by a suction blower which discharges the vapor-laden air to the recovery plant. The solvent-vaporizing operations may be conducted in locations at some distance from the recovery plant and the vapor-laden air collected from each operation drawn through the duct system to the recovery plant. Since these systems recover vapors which are present in extremely low concentrations in the air, they are designed so that sufficient air is drawn from the solvent vaporizing operation to keep the vapor-air mixture safe from fire or explosion hazard. This safe operating condition may be assured by automatic valves actuated by both air flow and vapor concentration. If for any reason the air flow to the recovery plant drops, or the vapor concentration in the air increases to a predetermined value, the solvent vaporizing operation is automatically stopped, or the vapor-laden air is vented to the atmosphere, or both.

Since the vapor-laden air which is collected usually carries dust or lint, it is passed through a suitable filter designed to remove effectively the type of solid material present. In many cases the filter medium is arranged so that it can be changed without stopping the air flow. This is a particularly important feature where the recovery plant must be operating continuously over long periods of time. If the vapor-laden air is at an elevated temperature, it is cooled indirectly by water.

The Columbia Activated Carbon System*

The modern Columbia Activated Carbon System of Carbide and Carbon Chemicals Corporation was made possible by the development during the first World War of a vapor-adsorbent, activated carbon for use in military masks to protect against toxic vapors. This devel-

* Data from A. B. Ray, Carbide and Carbon Chemicals Corporation.

opment was carried out by Dr. N. K. Chaney in the laboratory of the National Carbon Company, Inc., and is regarded by some as one of the outstanding scientific achievements of the last quarter century. The activated carbon originated to meet the wartime emergency has been tremendously improved and modified during the past twenty years. Recovery systems in operation in 1940 using Columbia Activated Carbon

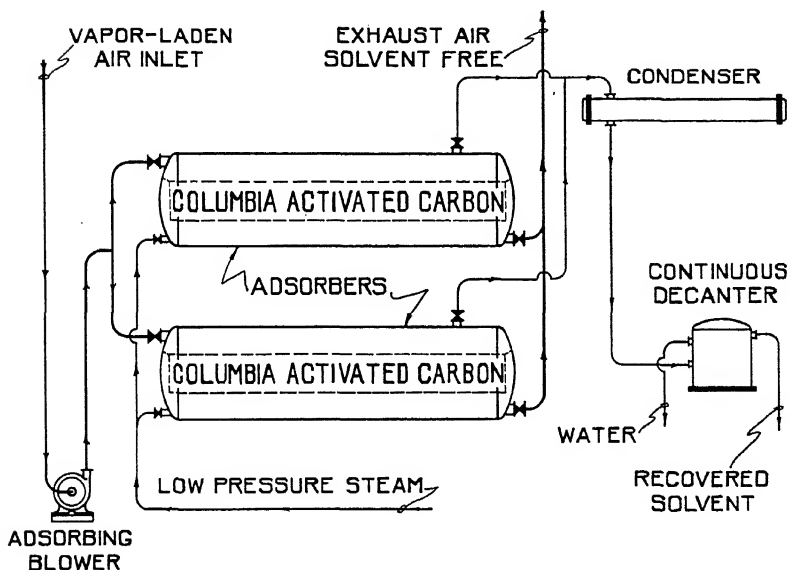
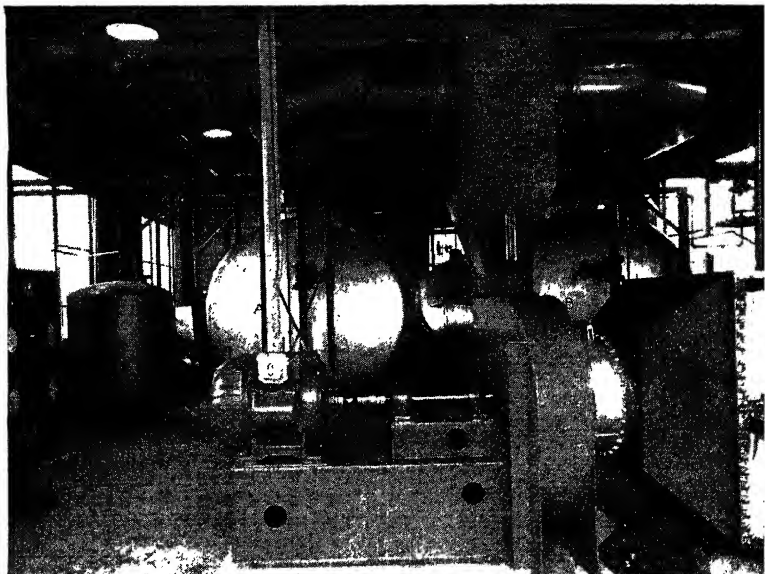


FIGURE 44.

recovered well over 400,000,000 pounds of solvents with a value of over \$15,000,000.

The operation of a simple type of Columbia Activated Carbon unit for continuous operation is shown in Figure 44. The filtered and cooled vapor-laden air is drawn under automatically controlled conditions from the solvent-vaporizing operation and is passed to the bed of carbon in one of the adsorbers (Figure 45).

The activated carbon adsorbs and holds the solvent vapor and the denuded air is discharged to the atmosphere. The passage of the vapor-laden air to the adsorber is continued until the carbon bed has adsorbed the desired quantity of solvent. If the vapor is passed to the carbon bed at a constant rate, the desired charge is obtained by keeping the adsorber in service for a definite period. If, however, as is most often the case,



Courtesy Carbide & Carbon Chemicals Corp.

FIGURE 45. General view of the two adsorber, manually operated recovery plant. Air enters through air cooler at right and is passed by blower in center to the adsorbers in background.

the vapor is passed to the adsorber at widely varying rates, the desired charge is obtained by means of a sensitive vapor detector in the air exhausted from a portion of the carbon bed, which indicates when the carbon has adsorbed its proper charge. When the carbon bed in one adsorber has become charged with

vapor, the vapor-laden air is either manually or automatically switched to the other adsorber.

The adsorbed solvent is then driven out of the charged adsorber by introducing low-pressure steam at a controlled rate below the carbon bed. The steaming is continued for from 15 to 60 minutes and then the adsorber is ready to be placed in service again. The steam passing through the charged carbon causes the release of the adsorbed vapor, and the steam-solvent mixture discharged from the adsorber is condensed. If the solvent is not appreciably soluble in water, it is



Courtesy Carbide & Carbon Chemicals Corp.

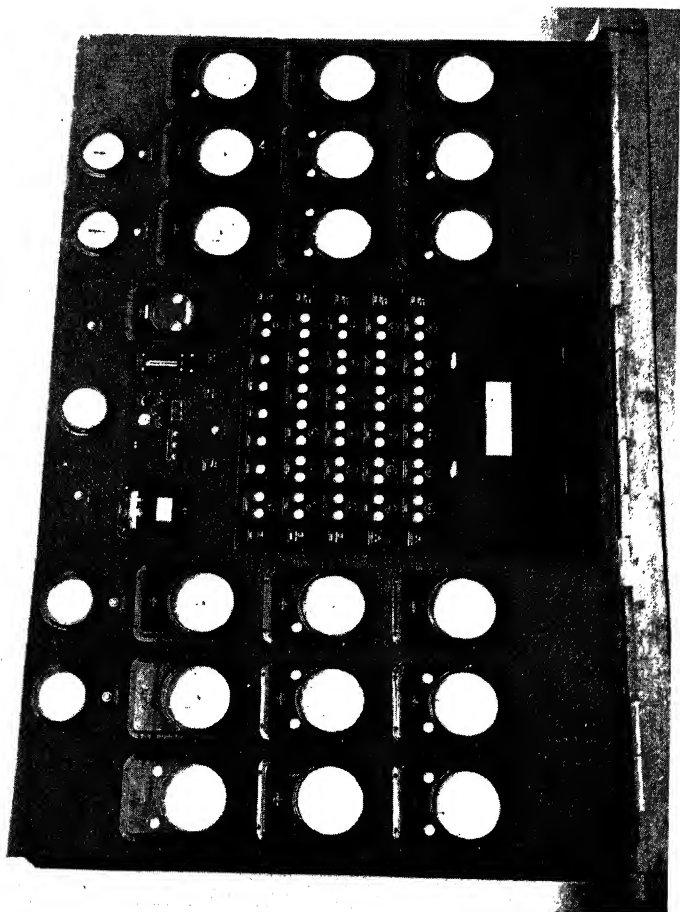
FIGURE 46. Typical horizontal adsorber ready for shipment.

separated from the water by an automatic continuous decanter. If the solvent is completely soluble in water, it is separated by distillation. If both types of solvent are present, a combination of the two processes is usually used.

The adsorbers which hold the carbon are probably the most important items of the equipment. They are either horizontal or vertical and have special internal fittings to support the carbon bed properly, to distribute the vapor-laden air and steam, to prevent condensation from wetting the carbon bed, and to prevent

FIGURE 47.
Instrument panel
used in a large, auto-
matically operated re-
covery plant.

*Courtesy Carbide &
Carbon Chemicals Corp.*



corrosion. A large adsorber of the horizontal type is shown in Figure 46 which is typical of the adsorbers installed in most plants where a relatively large volume of vapor-laden air is to be handled. In this type of adsorber the carbon may be placed in a single bed varying in thickness from 12 to 30 inches, or in specially designed multiple beds to obtain maximum bed area in a minimum space. Where corrosive conditions are to be met, stainless steels of suitable composition or other metals and alloys are used. Vertical adsorbers are used in small plants or where floor space is limited.

The valves which control the flow of vapor-laden air, steam, and solvent vapors are in many plants operated by hydraulic or pneumatic cylinders. The operation may be controlled automatically or manually from a central location. Such instruments as are required for the operation and control of the recovery equipment are installed on a centrally located panel (Figure 47). These instruments include recording thermometers, air flow meters, pressure gauges, vapor concentration detectors, and cycle controller. The air flow meter and vapor concentration detector on vapor-laden air may be set to control or vary the air flow as desired. The extremely sensitive vapor concentration detector may be used to switch adsorbers automatically or to signal the operator when one adsorber is charged. The cycle controller (Figure 48) automatically operates the plant on a fixed cycle or as determined by the break-point indicator. Signal lights on the instrument panel show the operating status at all times.

The expense of recovering solvents by this system depends upon the recovery conditions. The main items of operating expense are for steam, water, power, labor and maintenance. The steam requirement will range from less than three pounds to about five pounds per pound of solvent recovered. The high steam consumption is required when the recovered solvent must be redistilled to make it suitable for reuse.

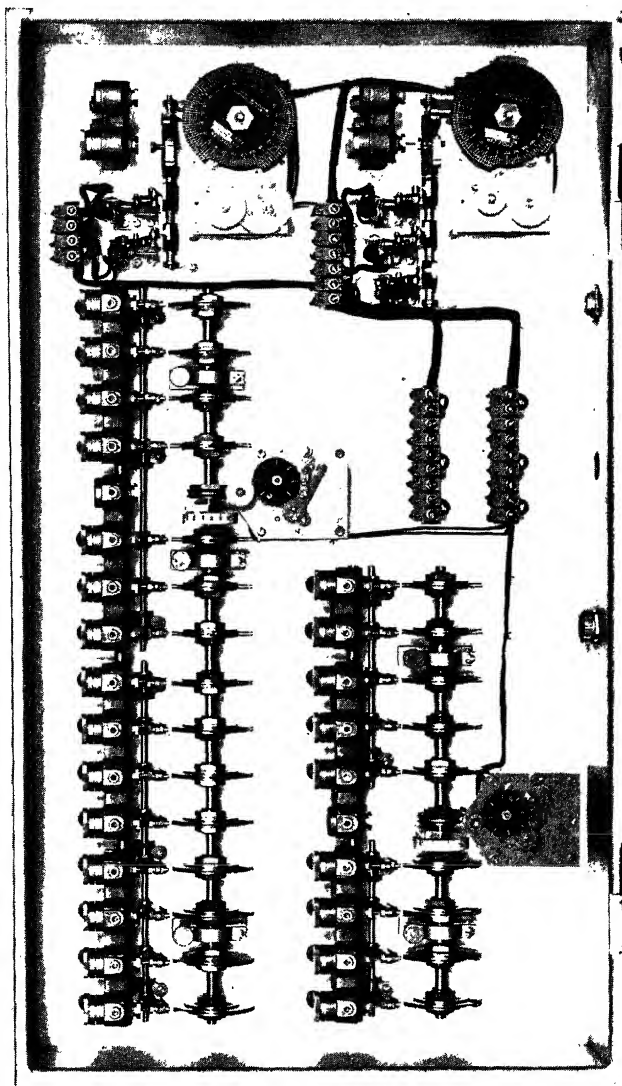


FIGURE 48. Cam system in cycle controller in a large, automatically operated recovery plant.
Courtesy Carbide & Carbon Chemicals Corp.

The consumption of electric power will vary with the concentration of the vapor in the air. In typical recovery plants where the concentration of the solvent vapor is 40 to 50 per cent of the concentration of the lower explosive limit, the power consumption is approximately 0.04 to 0.08 kwhr per pound of solvent recovered. The main power requirement is for drawing the vapor-laden air from the manufacturing operation and passing it through the recovery equipment. The water required for the recovery operations will depend upon the temperature of the vapor-laden air, the distilling operations required, and upon the temperature of the available water. For the recovery of a solvent such as benzol, the requirement of water at a maximum temperature of 70° F. is approximately seven gallons of water per pound of benzol recovered. For the recovery and redistillation of a solvent such as acetone, the requirement of 70° F.-water is about 9½ pounds per pound of acetone recovered.

The operation of a recovery plant is simple, one operator being sufficient even for large plants. The operating expense will vary with the cost of the utilities and the recovery conditions in general; but experience has shown that it may in some cases be as little as 0.2 cent per pound of solvent recovered and that it practically never exceeds one cent. A Columbia unit at the plant of a large manufacturer of rubber products gave the following operating costs:

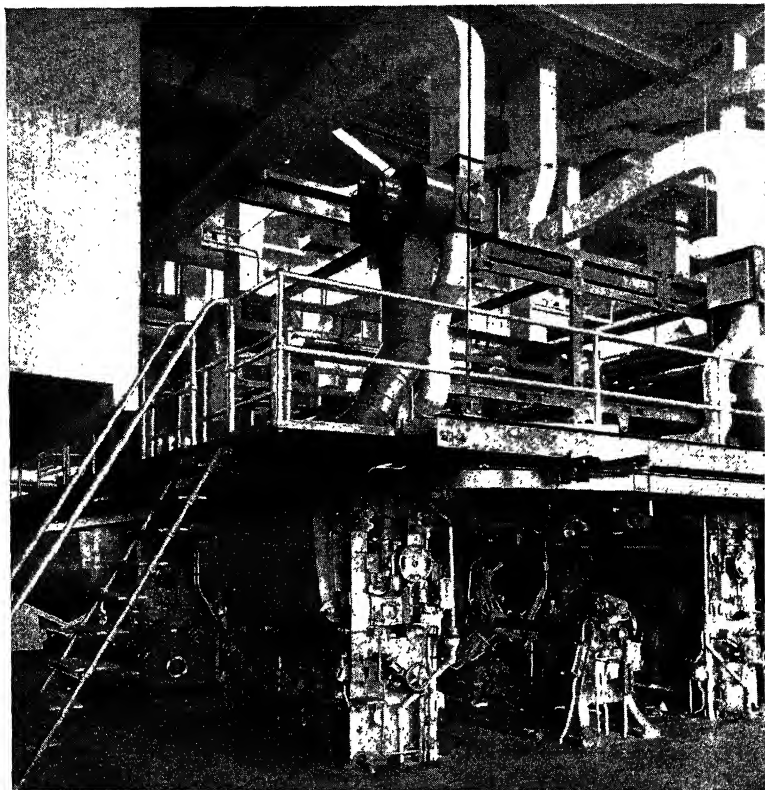
Volume of gases handled = 13,000 cubic feet per minute.

Temperature of entering gases = 165° F.

Average percentage of solvent recovered based on the solvent reaching the solvent recovery system = 99.7%.

Operating expense per pound of solvent recovered = \$0.0023.

In another plant recovering solvent used in the roto-gravure printing of newspapers where the solvent-laden air is low in solvent concentration, about 0.4 pound of solvent per 1,000 cubic feet of air, handling 22,500 cubic feet of air per minute, has a recovery



Courtesy Carbide & Carbon Chemicals Corp.

FIGURE 49. Vapor collecting system on high-speed rotogravure presses. Printed paper passes through drier at high speed. Air circulated through the drier vaporizes the solvent and the vapor-laden air is passed to the recovery plant through ducts.

efficiency of about 99 per cent for the recovery unit and about 83 per cent for the whole plant. This plant requires from 3.5 to 4.5 pounds of low-pressure steam per pound of recovered solvent, 10 gallons of 70° F.-cooling water and from 0.13 to 0.17 kilowatt-hour of electricity on the same basis.

A Columbia unit of large capacity was installed in 1926 to recover ether and alcohol from the manufacture

of rayon from nitrocellulose. This installation is still operating with original carbon and equipment. More recently, several large units were placed in operation to recover acetone from the manufacture of rayon from cellulose acetate, and these are operating successfully.



Courtesy Carbide & Carbon Chemicals Corp.

FIGURE 50. Duct system carrying vapor-laden air from rotogravure presses to solvent recovery plant. Small building houses automatic safety valve which vents directly to the atmosphere in an emergency.

Industries making use of this system include rayon, rubber, plastics and resins, coated paper and fabrics, cellulose products, dry-cleaning, grease and oil extraction, fermentation, petroleum products and numerous others, and the range of vapors profitably recovered includes almost every type of industrial solvent.

The Acticarbhone Activated Carbon System*

Just as the Columbia System previously discussed is the outstanding American system for recovery of vapors using activated carbon, the Acticarbhone System represents the outstanding accomplishments of European engineers in the field of solvent recovery using activated carbon. While it is not the oldest (a further

* E. L. Luaces, Dayton, Ohio.

point of resemblance with the Columbia System), it is the most widely used system for recovery of vapors with activated carbon in the entire world. Installations are found in more than thirty countries the world over, an accomplishment which has not been achieved by any other process using activated carbon for the recovery of vapors.

The Acticarbone Activated Carbon System was developed in France some twenty years ago as the result of the urgent need of Société de Recherches et d'Exploitations Petrolifères for a means of extracting gasoline from natural gas safely and efficiently with activated carbon. Particularly during the last decade it has developed very rapidly, and today it is found in practically every part of the world recovering all types of industrial vapors amenable to recovery by adsorption on activated carbon.

In its present state of development the process is extremely simple and safe in operation. The initial cost of the installation is decidedly lower than that of the older mechanical and liquid absorption systems. The operating costs are substantially lower and the efficiency extremely high. The solvent recovered is of the highest quality and does not have to undergo any purification (except rectification in the case of water-miscible solvents) before re-use, but perhaps the most attractive feature of the process is its ability successfully to operate with solvent vapor concentrations far beyond the effective range of the older processes.

Practical experience has shown that it is possible to operate with a high overall recovery yield when the concentration of solvent vapor in the vapor-laden air is from 5 grains per cubic foot down to 0.5 grain, and in extreme cases even as low as 0.09 grain per cubic foot. This makes it possible to aspirate large volumes of air, thereby increasing the captation efficiency of the installation and permitting the operation of the recovery plant itself with solvent vapor concentrations in the

solvent-laden air far below the lowest explosion limit. The factor of safety introduced thereby has resulted in many cases in a reduction of from 10 to 15 per cent in the insurance premiums paid. In at least one case the reported saving in insurance rates was 22 per cent.*

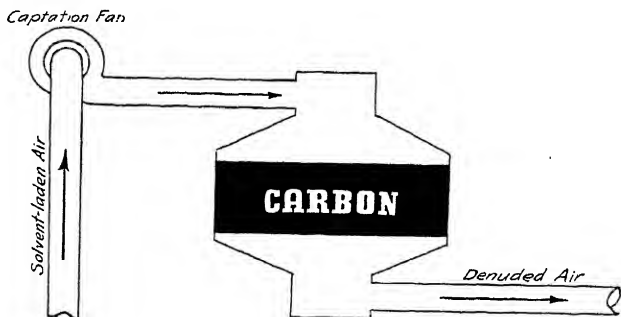
Since the per cent overall recovery efficiency is determined by dividing the total amount of solvent recovered for re-use into the amount evaporated, the most important factor in obtaining the highest overall recovery yield is the captation or collection of the solvent vapors. It is necessary to provide the equipment from which the solvent evaporates with suitably designed and fitted hoods or covers which will not make any part of the machine or apparatus inaccessible, or in any other way interfere with its operation. Once this has been done the rest is comparatively simple.

The recovery installation consists of suitable filtering apparatus having a specially designed compartment to arrest the propagation of any accidental spark or flame originating in the workrooms; the adsorbers containing the activated carbon; a condenser to condense the solvent vapors removed from the adsorbent, and a decanter to separate the solvent from the condensed steam when the solvent is immiscible with water. If the solvent being recovered is partly or wholly miscible with water, an automatic continuous rectifying column is provided with the installation.

The solvent-laden air, after being filtered to remove any dust or finely divided matter which it might carry in suspension, is propelled by the captation fan at a pressure of about 4 or 5 inches of water, through a bed of highly activated carbon held in the adsorber, as shown in Figure 51. The adsorption will go on for a period of from not less than 30 minutes up to several hours—or even a whole day or week for the smaller installations and those larger ones which are only operated during short intervals of time. When the *prac-*

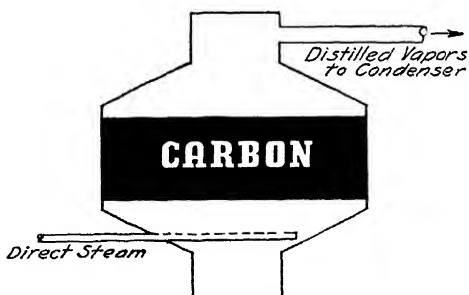
* Sedgewick, D. D., *American Printer*, April, 1936.

tical saturation point has been reached, the flow of solvent-laden air is diverted to the second adsorber and the first enters the second stage of the recovery process—regeneration or distillation.



Courtesy E. L. Luaces and Associates

FIGURE 51. The solvent-laden air is put through the activated carbon bed by the captation fan and the denuded air is evacuated outside the building or returned to the workrooms. A pressure of from 4 to 5 inches of water proves sufficient.

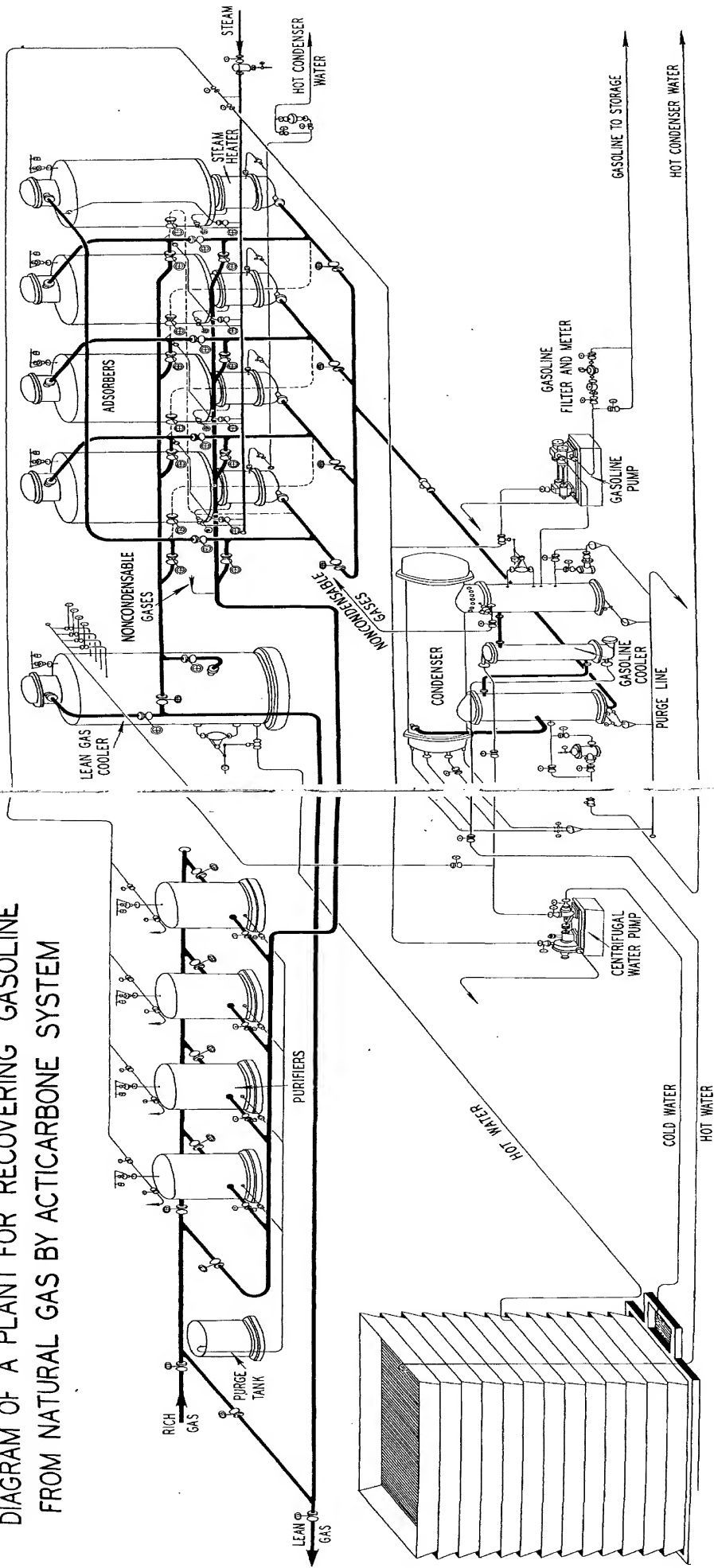


Courtesy E. L. Luaces and Associates

FIGURE 52. Steam is injected at the base of the adsorber to drive out or distill the adsorbed solvent. The vapors are taken off and condensed.

The purpose of regeneration is to remove from the activated carbon the vapors which it has adsorbed and is retaining in its pores. To this end the temperature of the activated carbon is increased sufficiently to distill out the adsorbed solvent. Regeneration, as shown in Figure 52, is carried out simply by injecting low

DIAGRAM OF A PLANT FOR RECOVERING GASOLINE
FROM NATURAL GAS BY ACTICARBONE SYSTEM



pressure steam directly into the adsorber and continuing the application until all of the adsorbed solvent has been vaporized and driven out. When this operation has been completed the activated carbon is quite moist due to steam condensation in bringing up the temperature of as poor a conductor of heat as activated carbon. Moisture is highly detrimental to solvent vapor adsorption and if left in the activated carbon its efficiency would suffer very definitely. For this reason the activated carbon is dried with warm air until all the moisture has been driven out and is then cooled down to room temperature with cooled air, as in Figure 53.

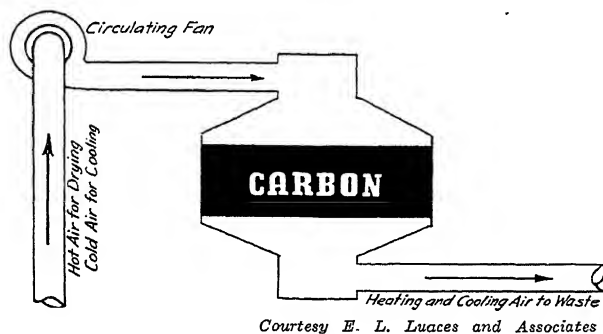
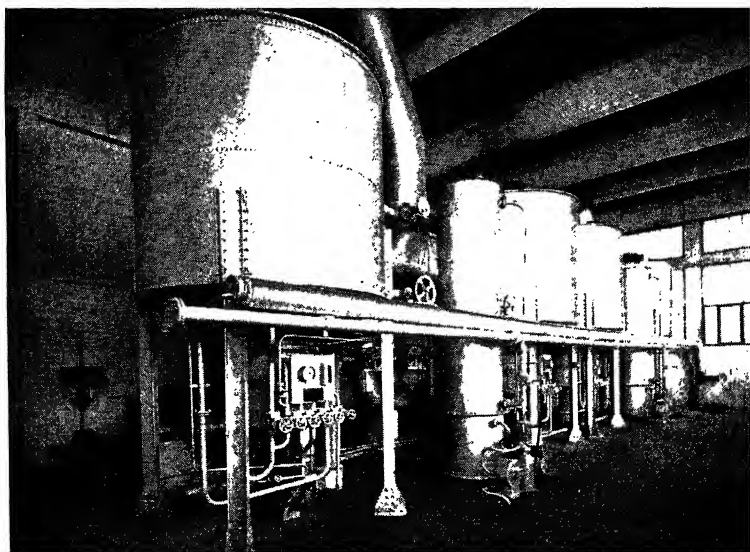


FIGURE 53. After steaming, the activated carbon is dried by passing warmed air through the adsorber. It is then cooled with air.

The distilled vapors are put through a suitable condenser forming part of the recovery installation. If the solvent is immiscible with water, as is the case with benzine, naphtha, benzene, trichloroethylene, etc., the decanter separates the water, which is discharged into the sewer, from the solvent, which is ready for re-use. If the solvent should happen to be miscible with water—as is the case in plants using ethyl acetate, alcohols, acetone, and similar solvents—the condensate is delivered to an automatic continuous rectifying column, where the solvent is separated from the water. In some cases a miscible and an immiscible solvent form

part of the solvent mixture used. In such cases, the decanter separates the immiscible solvent, and the water containing the miscible solvent is delivered to the rectifying column where the solvent is separated from the water.



Courtesy Acticarbene Corp.

FIGURE 54. Typical Duplex Four-adsorber Installation in a Dry-cleaning Plant.

While solvent recovery installations have been made with capacities as low as 10 gallons *per day*, there is no upper limit to the capacity for which an installation might be designed, and some in operation recover millions of gallons annually. Either single- or multiple-adsorber installations can be made. Where the amount of solvent to be recovered is very small the plant is designed to operate six, twelve or more hours without regeneration. In such cases the regeneration might be carried out during the lunch hour and at the close of day, or once only after working hours, depending upon

local conditions. Recovery plants using the Acticarbone System have been designed to operate fully automatically on a predetermined cycle without any attention whatever, and have been successfully doing so over substantial periods of time.

In most installations two adsorbers are used and perforce one is adsorbing while the second is being regenerated and cooled. When three adsorbers are used, one is adsorbing while the second is being regenerated and the third is being cooled. When four adsorbers are used, the operation is staggered so as to have two adsorbing—but reaching saturation at different times—one being regenerated and the fourth being cooled. Except in the extraction of gasoline from natural gas, more than four adsorbers are rarely used.

Examination of operating data accumulated over nearly two decades of practical use definitely shows that the Acticarbone Activated Carbon Recovery Process, when properly designed and operated, can effect such large savings that it will be amortized within a period of from six months to two years. The amount of labor required is negligible and except in those exceptional cases where it is necessary to place the recovery plant down in the cellar, up on the roof or in a building away from the workrooms where the solvent is evaporated, it is possible properly to attend to it without additional help. The operation is so simple and fool-proof that unskilled labor can be trained to run the installation properly, or full automatic control may be used for greater economy and efficiency.

These practical data also show that it is possible to recover for re-use from 97 to 99 per cent of the solvent vapor in the solvent-laden air and to attain overall yields up to 94 per cent of the solvent evaporated.

Other Activated Carbon Systems

It will be understood that there are other commercially important systems for recovery of vapors using

activated carbon, but it would be an impossibility fully to describe each one of them. As has previously been mentioned, the Columbia System and the Acticarbone System are representative of the best that the United States and Europe can offer. There is hardly any fundamental difference in the actual results obtained with the several recovery systems available to the public. There are, of course, minor differences in details of operation and construction, but these primarily reflect the personal preferences of the individual designers. There is within the industry a full interchange of patent rights, thus permitting each company to make use of the latest discoveries or developments of the others. Thus the art progresses rapidly, and industry and the public in general benefit thereby.

Chapter 14

Solvent Recovery by Condensation at Constant Pressure

Superheated Vapor

It has been pointed out in previous chapters that a volatile substance may exist in either the solid, liquid, or vapor state, and that it is possible under specific conditions to have one, any two, or all three forms of the substance present at the same time. Thus, if temperatures are high enough and pressures low enough, it is possible to have the substance entirely in the vapor state, for various combinations of temperature and pressure. Vapor under these conditions is in the superheated condition.

Saturated Vapor

If liquid and vapor are present together, the temperature may be varied, but the pressure (the vapor pressure of the substance) will depend upon the temperature. Or the vapor pressure may be varied and the temperature of the substance will change correspondingly. The relation between the temperature and the vapor pressure gives the vapor pressure curve for the liquid.

If all three forms of the substance are present at the same time, neither the temperature nor the pressure can be varied, because the three can exist together only at one specific temperature and pressure. Thus, ice, water, and water vapor can exist together at approximately 0° C. and 4.6 mm. pressure.

Example 18. Cotton cloth from a dry-cleaning operation contains liquid benzol (benzene, C_6H_6). It is desired to remove the benzol from the cloth and to recover it.

(a) The cloth is introduced into an air-free, completely evacuated, chamber, *A*, at a temperature of $20^\circ C.$ ($68^\circ F.$) at which temperature benzol has a vapor pressure of 74.7 mm. The benzol will immediately start to vaporize. This will require heat (latent heat of vaporization). If the heat is not forthcoming from the surroundings, the heat will be furnished by the liquid benzol itself which will therefore drop in temperature. If, on the other hand, heat is furnished from the surroundings rapidly enough to keep the temperature at $20^\circ C.$, the benzol will continue to vaporize until the whole chamber is filled with benzol vapor at the pressure of 74.7 mm.

Suppose now that an exhausting pump, *B*, is started. The benzol vapor will be removed by it, thus tending to lower its

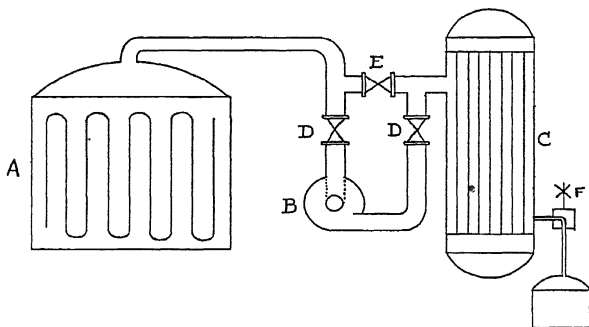


FIGURE 55. Diagram Illustrating Solvent Recovery by Simple Condensation.

pressure in the chamber. As soon as this occurs, more of the benzol will vaporize, and the process will continue until all the liquid has vaporized.

The benzol vapor exhausted by the pump may be discharged into a condenser, *C*, at substantially the same pressure at which it existed in the vaporizing chamber. Suppose that the tubes in the condenser are at a temperature of $10^\circ C.$ ($50^\circ F.$) at which temperature the vapor pressure of benzol is 45.4 mm. The vapor coming into contact with the tubes can exist only when its pressure is 45.4 mm., and therefore, so that the pressure may fall from 74.7 to 45.4 mm., some of the benzol condenses. This condensation gives out heat which must be absorbed by the cooling water in the tubes, or the temperature of the cooling surface will rise. It is therefore necessary to supply more cooling water to keep the temperature at $10^\circ C.$ As rapidly as the vapor con-

denses, fresh vapor furnished by the pump arrives, and the process continues until all the benzol on the cloth has evaporated.

Suppose now that the exhauster has been replaced by an open pipe, by closing the valves *D*, *D*, and opening the valve *E*. The pressure in the vaporizing chamber was 74.7 mm. and that at the surface of the condenser was 45.4 mm. A difference in pressure between these two points would have caused the vapor to flow from the cloth to the condenser, and the evaporation would therefore have continued as before without the aid of a pump as long as there was a difference in temperature between the cloth and the condenser.

(b) The benzol-laden cloth is introduced into a chamber containing air at 20° C. and at atmospheric pressure (29.92 inches or 760 mm.). The pressure of the air does not appreciably affect the partial pressure of the benzol, which remains at 74.7 mm. Since, however, the benzol vapor will occupy space, either some of the air must be removed from the chamber or the total pressure in the chamber will rise until it has reached 834.7 mm., which is the sum of 760 (the partial pressure of the air) and 74.7 mm. (the partial pressure of the benzol). Suppose that the air is removed by opening the air vent valve, *F*, to keep the total pressure constant at 760 mm.; then the partial pressure of the benzol will still be 74.7 mm. and that of the air will be 685.3 mm., which is the difference between 760 and 74.7.

Under these conditions the mol fraction of the benzol in the air-benzol mixture will be

$$\frac{74.7}{760} = 0.0983$$

and the percentage by volume of the benzol in the air will be 9.83.

The weight percentage of benzol in the air mixture is calculated as follows:

$$\begin{array}{rcl} \text{Molecular weight of benzol} & = & 78 \\ \text{Molecular weight of air} & = & 29 \end{array}$$

In 100 mols of mixture there are 9.83 mols of benzol and 90.17 mols of air. The weight of each of these will be:

$$\begin{array}{rcl} 9.83 \times 78 & = & 767. \\ 90.17 \times 29 & = & 2615. \\ \hline \text{Total} & = & 3382. \end{array}$$

$$\text{Weight percentage of benzol} = \frac{767 \times 100}{3382} = 22.7\%$$

The weight of benzol in one cubic foot of the mixture is calculated as follows:

100 pound mols of the mixture contain 767 lbs. of benzol.
 100 pound mols of a gas occupy at standard conditions
 11×359 cu. ft., or

$$100 \times 359 \times \frac{(273 + 20)}{273} = 38,500 \text{ cu. ft. at } 20^{\circ} \text{ C.}$$

Therefore the pounds per cubic foot will be

$$\frac{767}{38,500} = 0.0199$$

The presence of the air will not affect the condensation at the condenser, except that it interferes with the flow of heat from the condensing vapor to the surface of the cooling tubes. The partial pressure of the vapor is reduced at the surface to 45.4 mm., making the total pressure there

$$45.4 + 685.3 = 730.7 \text{ mm.}$$

Since this is less than the pressure of 760 mm. in the chamber, the gas mixture will tend to flow in the direction of the condenser, and the condensation will continue as before. It is probable, however, that in such an apparatus, the air remains practically stationary except as convection currents due to heating and cooling may be set up, and that the benzol vapor actually passes through the air from the cloth to the condenser by diffusion, which is of course a very slow process. It is therefore true that solvent recovery in the absence of air or other non-condensing gases is much more rapid than when air is present, unless the apparatus is designed to permit vigorous circulation of the air between the cloth and the condenser. The residual benzol left in the air at 45.4 mm. pressure will not be condensed.

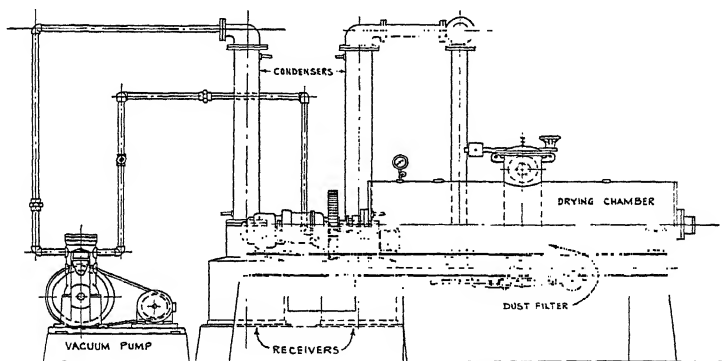
Stokes Vacuum Apparatus

An example of this method of solvent recovery is shown in the Stokes Vacuum Solvent Recovery Apparatus illustrated in Figure 56. This apparatus is suitable for the recovery of alcohol from the dregs of extract-making, the removal of benzol from rubber-impregnated materials, the removal of solvent from wood chips after rosin extraction, and for similar purposes. It consists of a steam jacketed cylindrical drum *A*, in which the material containing the solvent is brought into contact with the hot walls by means of a suitable stirring device driven by the gearing, *B*.

The apparatus, after charging, is put under a vacuum by means of the vacuum pump, *C*, which is

joined to the drum by a dust collector, *D*, and the surface condenser, *E*.

The air leaving the apparatus will be saturated with solvent at the temperature of the condenser, *E*, and since under a high vacuum the gas exhausted may consist largely of uncondensed vapor, the gas is delivered from the pump to another surface condenser, *F*, where the gas is under atmospheric pressure and the bulk of the solvent vapor passing through the pump will be condensed.



Courtesy F. J. Stokes Machine Co.

FIGURE 56. Stokes Vacuum Solvent Recovery Apparatus.

Mixture of Condensable Vapors

The foregoing has referred to a single condensable vapor. Suppose now that the solvent to be vaporized and condensed is composed of a mixture of two or more liquids of different boiling points and vapor pressures.¹ While the liquid is vaporizing, the residual liquid is becoming increasingly richer in the less volatile components, the vapor pressure of the mixture is constantly decreasing, and therefore the weight of vapor per unit volume of air is growing less, until when the last of the solvent vaporizes, it consists wholly of the least volatile

¹ The reader is referred to Chapters 4 and 6 for the behavior of such mixtures during vaporization and condensation.

component, and its partial pressure in the air is that of this particular component, as if it alone had been present during the vaporization.

This gradual decrease of the concentration of the solvent vapor in the gas is not especially serious when mixtures of substances of similar volatility are being vaporized, but when the solvent consists of a mixture of substances with widely different boiling points, this factor is of considerable importance. For example, when gasoline, which is a mixture of hydrocarbons with boiling points ranging from 50 to 300° C., is used as a solvent, it is extremely difficult to remove its last traces, since they consist of substances of low volatility and the amount of them which will be carried off per unit volume of air is very small, except at high temperatures.

Thus the vapor pressure of gasoline which starts to boil at 50° C. may be calculated for a temperature of 20° C. by the method given in Chapter 3.

$$\begin{aligned} \log_e \frac{760}{p_2} &= \frac{L}{1.99} \left(\frac{1}{273 + 20} - \frac{1}{273 + 300} \right) \\ \text{where } L &= 20.5 \times (273 + 50) = 6600. \\ \log_e \frac{760}{p_2} &= \frac{6600}{1.99} (.00341 - .00309) = 1.065 \\ \frac{760}{p_2} &= 2.9 \\ p_2 &= 262. \text{ mm.} \end{aligned}$$

Therefore at 20° C., at the start of the vaporization, the weight of gasoline contained in one cubic foot of the air-gasoline mixture would be (assuming gasoline to have an average molecular weight of 125)

$$\frac{262}{760} \times \frac{125}{359} \times \frac{273}{(273 + 20)} = 0.11 \quad \text{foot.}$$

And at the end of the evaporation, when the component boiling at 300° C. was being vaporized alone, the weight of gasoline per cubic foot would be calculated in the same way, as follows:

Vapor pressure of the solvent at 20° C.

$$\begin{aligned} \log_{10} \frac{760}{p_2} &= \frac{L}{1.99} \left(\frac{1}{(273 + 20)} - \frac{1}{(273 + 300)} \right) \\ L &= 20.5 \times (273 + 300) = 11,750. \\ \log_{10} \frac{760}{p_2} &= \frac{11,750}{1.99} (.00341 - .00174) \\ \frac{760}{p_2} &= 18,500. \quad p_2 = 0.041 \text{ mm.} \end{aligned}$$

Therefore at 20° C., at the end of the vaporization, the weight of gasoline per cubic foot would be

$$\frac{.041}{760} \times \frac{125}{359} \times \frac{273}{(273 + 20)} = .0000175 \text{ lb. per cu. ft.}$$

Or in other words, at the start, 9.0 cubic feet of mixture will be required to carry one pound of gasoline, while at the end nearly 60,000 cubic feet are necessary.

Of course the obvious answer to such a question is the use of gasoline with a much shorter boiling point range, a special cut for the purpose.

Chapter 15

Condensation With Cooling Water

Types of Condensation

Solvent vapors may be condensed by the removal of heat at the condensation temperature in two ways, *i.e.*, by direct cooling or by indirect cooling. Direct cooling consists of bringing the vapor into direct contact with the cooling medium, as in the jet condenser. Indirect cooling introduces a dividing wall between the vapor and the cooling medium, as in the surface condenser. The direct cooling method is divided into two classes, first where the condensing vapor is soluble in the cooling medium, and secondly, where it is insoluble. The first class comes under the general subject of solution by scrubbing and will be discussed in detail in another chapter. The second class may be properly considered at this point.

Direct Cooling

Benzol is practically insoluble in water. Therefore if benzol vapor is brought into contact with water at a temperature lower than that of the vapor itself, flow of heat from the vapor to the water will occur, with condensation of the vapor and rise in temperature of the water. If sufficient water is present to prevent its reaching vapor temperature, all the vapor will condense, and there will issue from the condenser a mixture of benzol and water which, unless emulsification has occurred, will separate on standing, and the layer of benzol may be separated from the water layer by decantation. Direct-acting condensers of the type used

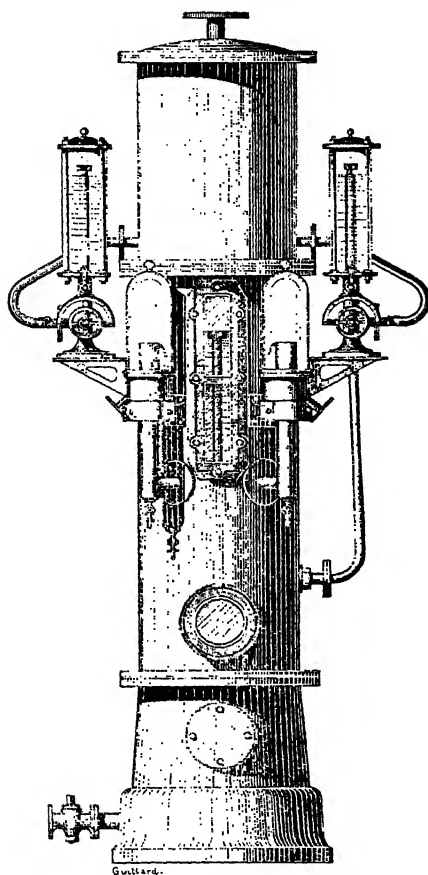


FIGURE 57. Continuous Decanter.

for condensing steam are in general suitable for this work.

In case the solvent recovery apparatus is to work under a vacuum, the jet condenser may be of the barometric type, or of the wet vacuum pump type.

Condensers similar to tower scrubbers are also suitable, the plate type or the tower filled with coke, rock, or other filling material being used. Those are, how-

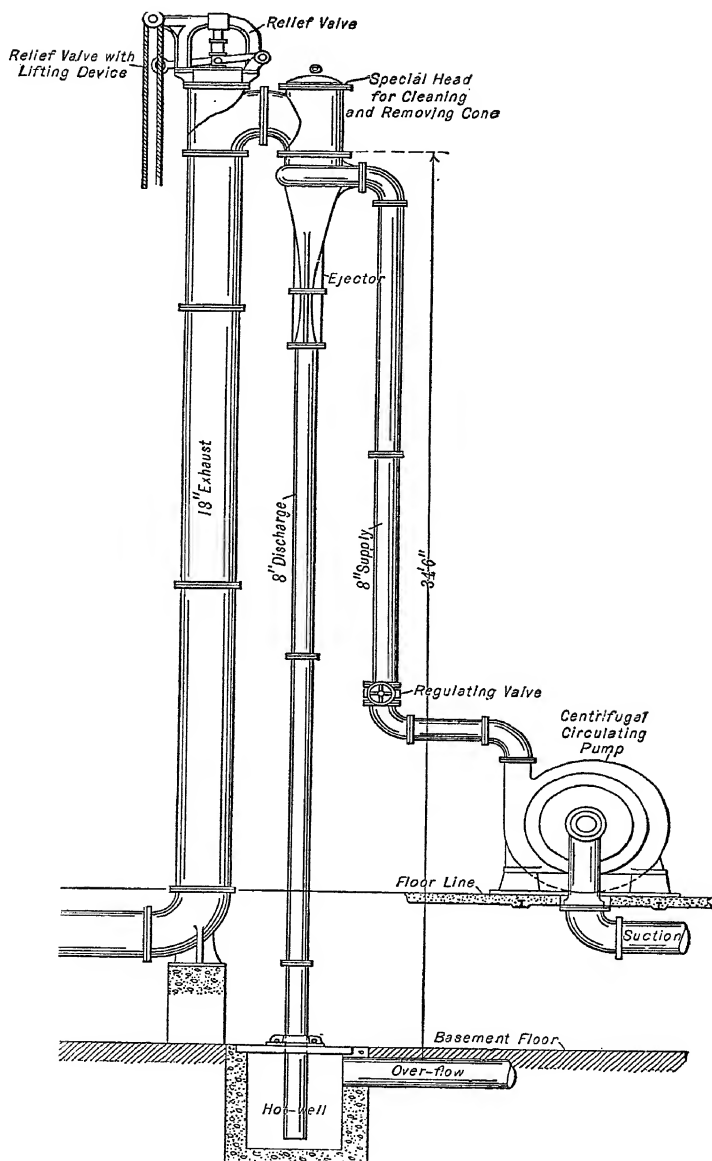


FIGURE 58. Barometric Condenser.

ever, better suited for the condensation of vapor when contained in air or other gases and are almost exclusively used under these circumstances where direct cooling is desired.

Water velocities in jet condensers are usually in the neighborhood of from 5 to 10 feet per second. In plate and filled type towers the average velocity of the water flowing down through them is from 1 to 3 gallons per minute per square foot of cross-section of the tower.

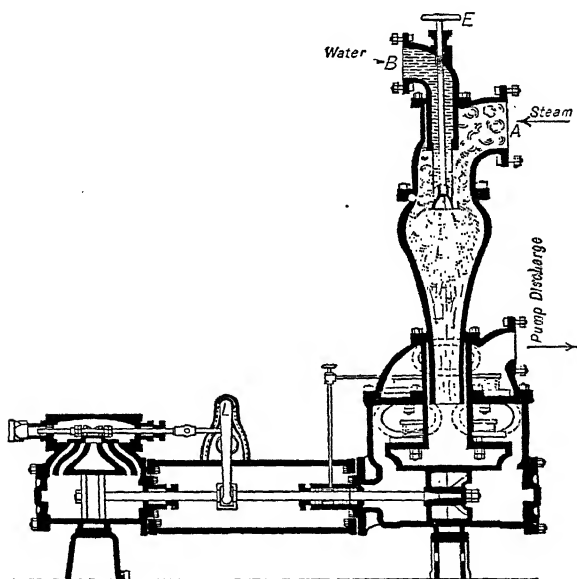


FIGURE 59. Jet Condenser with Wet Vacuum Pump.

When mixtures of condensable vapors and non-condensable gases such as benzol vapor in air are used in direct coolers, it is necessary to remove the gas from the cooler after the vapor has been condensed, by some suitable exhausting pump. In the case of towers and counter-current jet condensers, the gases are removed at the top, whereas in vacuum jet condensers using a wet vacuum pump, the air is removed by that pump.

The latter type is therefore used when the percentage of gases in the vapor is relatively small.

Indirect Cooling

Indirect or surface coolers and condensers are used when the solvents are water-soluble, or when it is desired to keep insoluble solvents dry and out of contact with water. The latter is difficult even with surface condensers, as moisture in the air will frequently condense simultaneously with the solvent vapor. Surface condensers are also used with insoluble solvents when the amount of solvent in the air is small, in order to avoid the mechanical difficulties of separating by decantation a small amount of solvent from a large amount of water. The objection to the use of direct cooling with soluble liquids is the necessity of using distillation as another step in the final recovery of the solvent.

The factors entering into the design of coolers will be discussed in a later section. The chief things to be remembered in the selection of a surface cooler are that the velocities of the water and the vapor should be as high as possible without undue friction or back pressure; that it should be counter-current; and that there should be no opportunity for the formation of dead spaces or pockets for stagnant fluid. Where dirty cooling water is used, the water surfaces should be easily accessible for cleaning.

The simplest type of cooler consists of a coil through which water is passed, fastened against the wall of the condensing chamber. This type is least expensive per square foot of heating surface for small installations, but is not easily arranged for high air or vapor velocities and is therefore not very efficient. Also, it is very bulky.

A similar type is the double pipe cooler or condenser, familiar to users of refrigeration apparatus. This type has great capacity per square foot of cooling

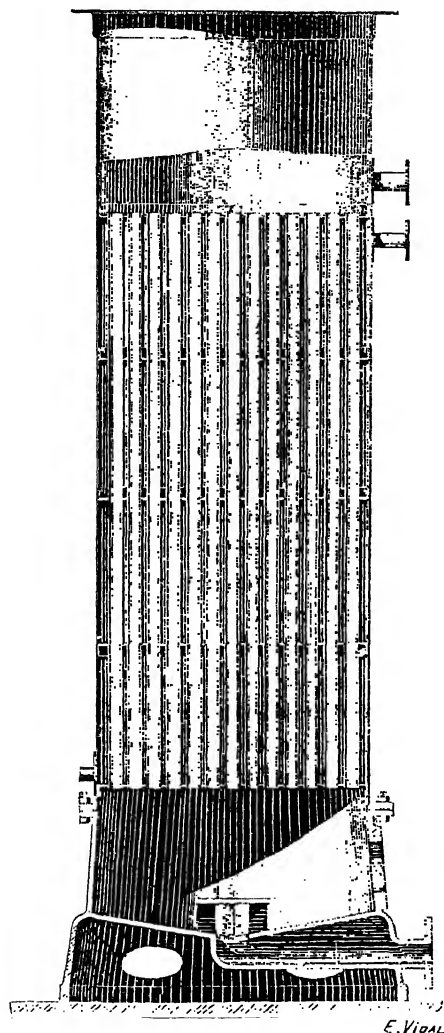


FIGURE 60. Simple Tubular Cooler.

surface on account of the possibility of obtaining high liquid and vapor velocities and it can be constructed easily out of stock fittings, but it is bulky and expensive to install.

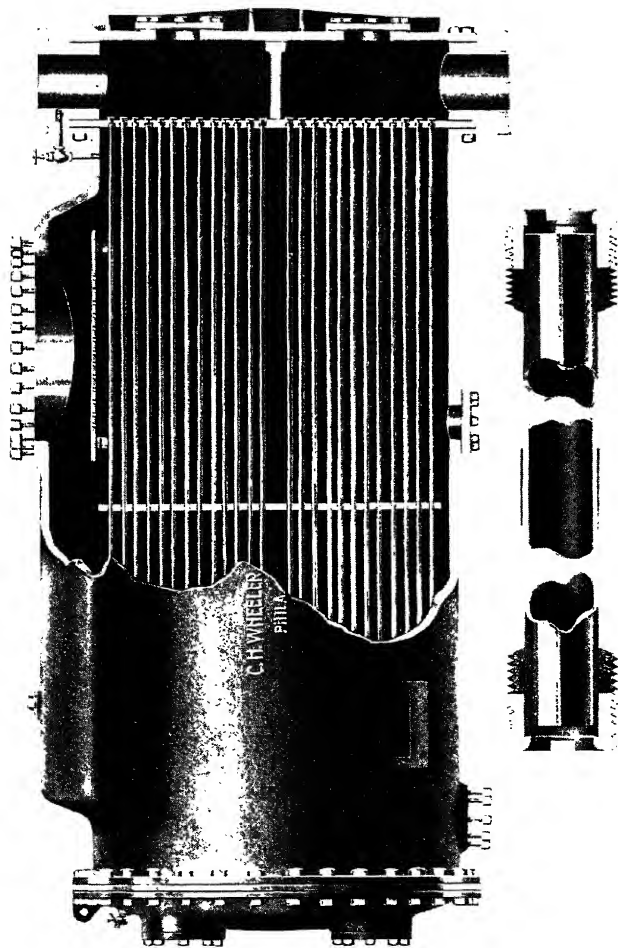
A third type of surface cooler is the tubular condenser. These are relatively inexpensive per square foot of cooling surface, but are of small capacity, as it is difficult to get high fluid velocities around the tubes. In order to accomplish this, the tubular coolers are often made multi-pass, which increases their capacity at increased cost per square foot of heating surface by increasing fluid velocities (Figure 61).

Cooling Water

Cooling water for condensers should be abundant and at low temperature. In many solvent recovery operations the efficiency of the recovery depends largely upon the ability to cool the gases to low temperatures, which means having cooling water at low temperatures and in considerable amounts to avoid undue temperature rise. Some plants are fortunately located as to water, having abundant supply at low temperatures both summer and winter. Other plants are not so well situated, and restrictions as to quantity and temperature, especially in the summer, place real handicaps on efficient solvent recovery operations. For such, methods of reusing and recooling the cooling water are of great importance.

There are two methods in common use for recooling water, both depending upon the evaporation of part of the water into air, the heat of vaporization effecting the cooling of the remainder. The evaporation and therefore the cooling obtained under these circumstances depend upon the temperature and the humidity of the air, best results being in general obtained when the air is relatively dry, although it is possible to cool water with saturated air. If water at any temperature whatever is brought into contact with sufficient quantities of air at 120° F. and 5 per cent humidity (which is the condition said to exist at times in the desert regions of the Southwest), both the water and the air can be cooled to wet-bulb temperature, which is about 70° F.

FIGURE 61.
Two-Pass Condenser
of the Type Suitable for
Solvent Recovery.



Such cooling is obtained by the use of spray ponds or cooling towers, the use of cooling ponds without sprays requiring such large areas (the water losing 2 to 4 B.t.u per square foot of pond surface per degree Fahrenheit temperature difference between the water and the air, plus or minus several hundred per cent depending upon atmospheric conditions) that they are economical only under very special circumstances.

Humidity Chart

In order to estimate cooling of water by air, the use of a humidity chart is required, such as Figure 62.

On this chart the curve marked 100 per cent relative humidity gives the weight of water expressed as pounds per hundred pounds of dry air which saturated air will hold at the temperature in question. For instance, saturated air at 70° F. will contain 1.55 pounds of water vapor per one hundred pounds of dry air. If the air, on the other hand, has a relative humidity of 50 per cent, it will contain 0.77 pound as read from the 50 per cent curve.

The curves running at about right angles to the humidity curves are adiabatic cooling curves. For instance, when water is brought into contact with air at some specific temperature and relative humidity, for instance 78° and 50 per cent, the air will fall in temperature along the adiabatic curve, up to the left, until the 100-per cent line is reached at 65°, which is the wet-bulb temperature. Adiabatic cooling implies no heat lost to or recovered from the surroundings. If the water is left in contact with the air, it too will eventually reach the wet-bulb temperature of the air if present in suitable amount, but cannot be cooled below that point which is the end of adiabatic evaporation.

It is obvious that the portion of the water which is evaporated in cooling the remainder is lost, as far as reuse is concerned, and must be made up by fresh

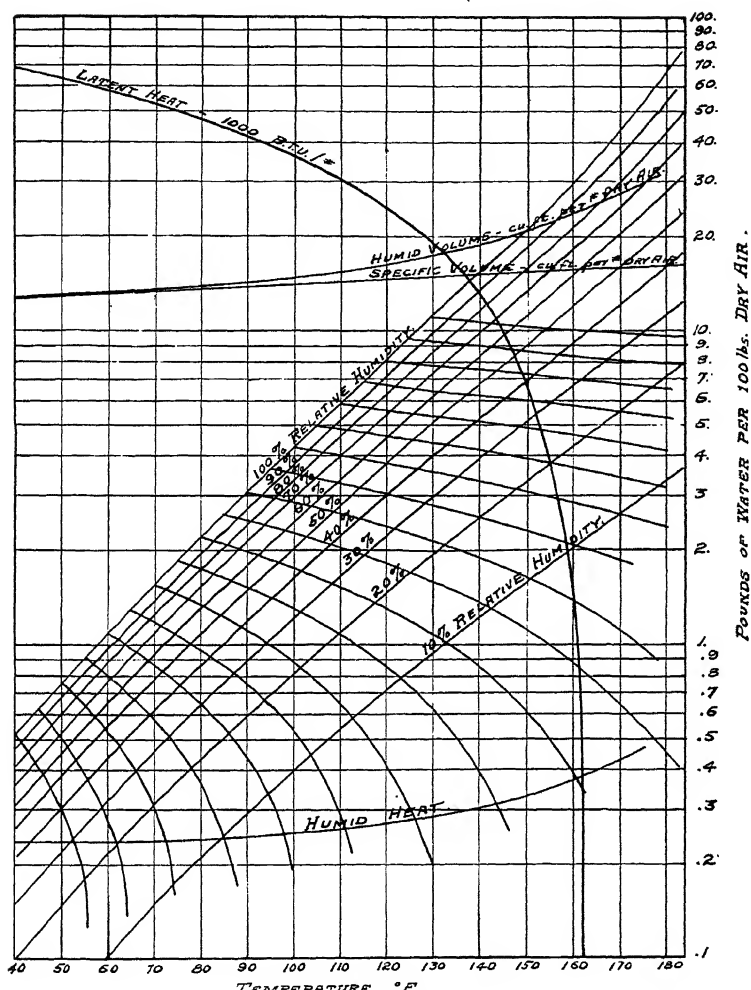


FIGURE 62. Humidity Chart.

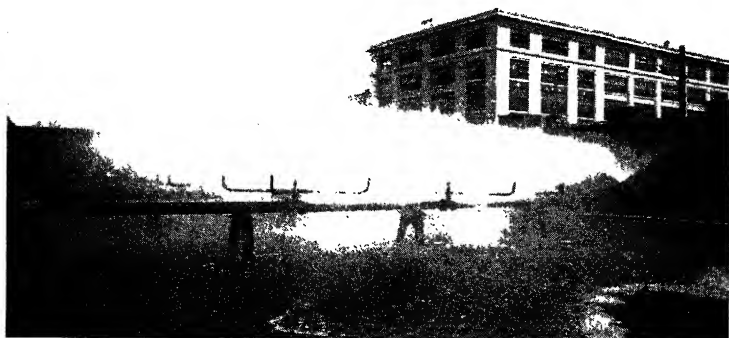
water. This loss will vary according to conditions, but averages between 0 and 5 per cent in most cases.

Spray cooling ponds of the type shown in Figure 63 require approximately 2 to 4 square feet of area for each gallon of water sprayed per minute, the water

being pumped against a pressure of about 6 to 7 pounds per square inch in order to operate the spray nozzles. Cooling may be improved by respraying the water. Water losses due to evaporation and entrainment amount to less than 3 per cent of the water sprayed.

Atmospheric cooling towers of the type shown in Figure 64 have approximately the following dimensions:

Gallons of water per minute	Ground area (square feet)	Height (feet)
100	11 × 17	20
300	19 × 25	30
500	19 × 37	30
700	19 × 48	30
1000	19 × 66	30



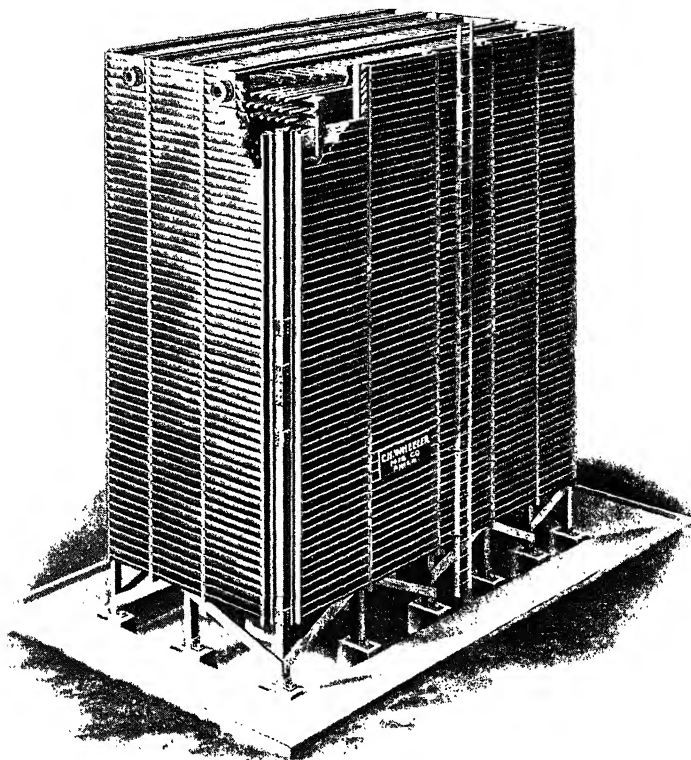
Courtesy Spray Engineering Co.

FIGURE 63. Spray Cooling Pond.

Such towers should cool the water to within 2 to 20° F. of the wet-bulb temperature depending upon atmospheric conditions. The power consumption of these towers is that consumed in pumping the water to the top of the tower.

Forced-draft towers of the type shown in Figure 65 are usually designed on the basis of 6.5 gallons of water per square foot of ground area of tower per minute, and will cool to within a few degrees of wet-bulb tem-

perature, depending on the height of the tower, standard towers being 25-30 feet high. The power consumption will be that required in pumping the water to the top of the tower plus that necessary to blow the air



Courtesy C. H. Wheeler Co.

FIGURE 64. Atmospheric Cooling Tower.

through the tower, the two amounts being approximately equal.

This type of tower gives difficulty in northern latitudes on account of ice formation on the fans in winter.

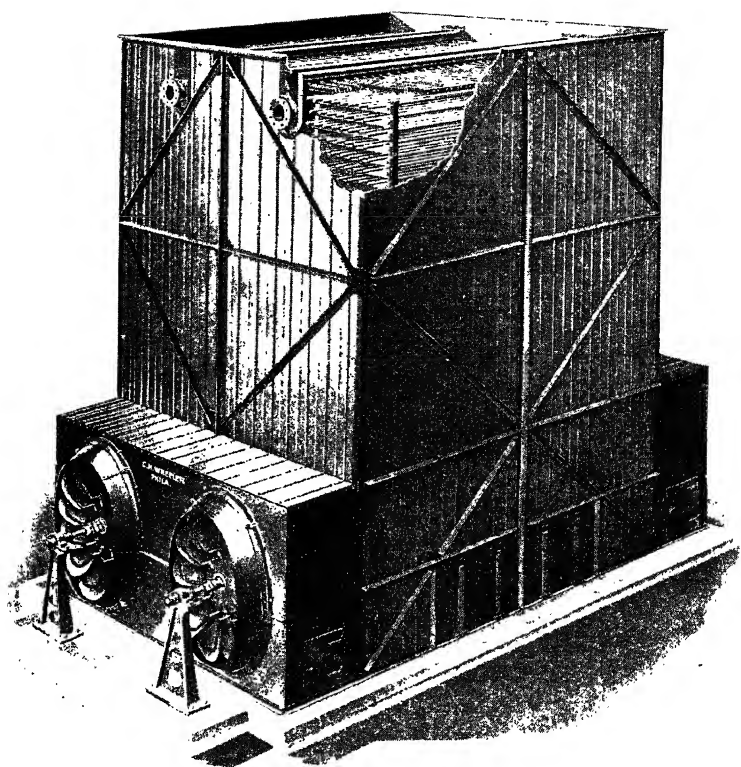


FIGURE 65. Forced Draft Cooling Tower.

Chapter 16

Cooling With Refrigeration

It frequently happens that the temperature required to remove the solvent vapor from the gas in which it comes from the vaporizing chamber is lower than can be obtained by the use of cooling water. Under such circumstances artificial cooling by mechanical refrigeration is used. It is not usually advisable to attempt the cooling of vapor-laden gases entirely by refrigeration if they are at a temperature considerably above the temperature to which the gases will finally be cooled, but it is better to cool as much as possible with water, and then finish with refrigeration. In small installations, however, it will prove more economical to do all the cooling with refrigeration to avoid excessive first cost of double cooling equipment.

The technique of cooling by means of mechanical refrigeration is similar to that of water-cooling. It should be borne in mind, when low temperatures are desired, that the presence of much moisture in the vapor-laden gases frequently causes trouble due to the formation of ice on the cooling surfaces, with the subsequent insulation against flow of heat. This trouble can be avoided only by the use of dried gases in the recovery apparatus, which is not often warranted, the cure being more expensive than the original trouble.

While there are many methods of obtaining mechanical refrigeration, in general, four are used. The first of these is the compression and subsequent expansion, performing work in a cylinder or turbine, of air or some inert gas. The second consists in the compression and condensation of some readily condensable vapor such as ammonia, carbon dioxide, or sulphur dioxide, and

the subsequent expansion to the vapor state through a throttling valve. The third makes use of the solubility of such vapors in some less volatile liquid such as water, by absorption under low pressure and revaporization under high pressure, a process of condensation and expansion as before. These systems are known as the dense air, the compression, and the absorption systems respectively. For detailed information on these systems, the reader is referred to "*Mechanical Refrigeration*" by MacIntire (Wiley) and to Marks, "*Mechanical Engineer's Handbook*" (McGraw-Hill).

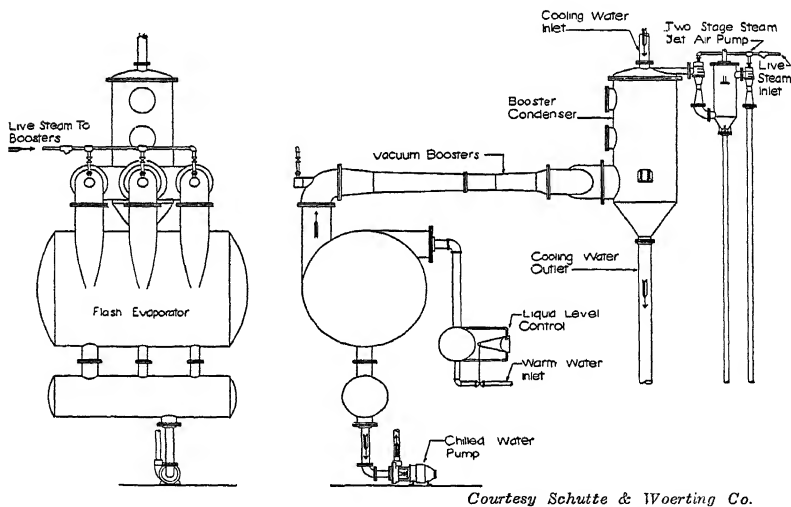


FIGURE Steam Jet Vacuum Refrigeration Apparatus.

The fourth method of artificial refrigeration makes use of the fact that in the adiabatic evaporation of water the latent heat cannot come from the surroundings and the water must therefore cool off in proportion to the amount that it evaporates. In operation, the water is placed in an insulated tank which is connected with a vacuum pump and the pressure is reduced by pumping off the water vapor. This causes the evapo-

ration of the water as soon as the pressure falls below the vapor pressure of the water, thus cooling the water and lowering the pressure still further. The process is limited only by the capacity of the vacuum pump and by the fact that water freezes at 32° F. In practice it has been found that 40° F. is about the lowest temperature that can be readily obtained, and that the simplest way to reduce the pressure is with the steam jet vacuum pump. Figure 66 shows a diagram of such an apparatus. Considerable steam is needed to operate such a pump and from three to four times the weight of the steam is needed in the form of cooling water to condense it.

Chapter 17

Heat of Vaporization in the Absence of Gases

Vaporization of a solvent in the absence of gases will occur when the temperature of the solvent is raised to such a point that the vapor pressure of the liquid becomes equal to the external pressure on the liquid. It will then continue at that temperature as long as the vapor is removed from the liquid and the heat of vaporization is supplied.

Heating by Direct Contact

The heat of vaporization may be transmitted to the liquid by direct contact of the liquid with a suitable heating surface. Thus the water in a boiler receives its heat from contact with the hot flues. Where a solid comes into contact with a hot surface, it is assumed that the flow of heat from that surface to the solid is very rapid, and that the diffusion of the heat through the solid to the interior is relatively slow. It is therefore necessary to insure continual and frequent contact between fresh, cold surfaces of the solid with the heating surface, which is usually accomplished by agitating or tumbling the solid around in its container.

In the case of a boiling liquid, the flow of heat from the solid heating surface to the liquid depends chiefly upon the velocity with which the liquid passes over the surface, the temperature difference, and the viscosity of the liquid. No accurate information is available at

the present time for calculating this. Where the boiling liquid is water, the coefficient of heat conductivity will depend upon the pressure, velocity, and arrangement of heating surface, and will vary perhaps from 400 to 1000 B.t.u. per square foot per hour per degree Fahrenheit temperature difference between the solid and the liquid. For more viscous liquids, the value will be lower, being probably inversely proportional to the velocity relative to water under similar conditions.

Heating by Radiation

The heat of vaporization may be transmitted to the vaporizing solvent by direct radiation through space from steam coils or other hot surfaces. The rate of flow of heat by radiation is given by the formula (Stefan-Boltzmann):

$$(28) \quad \frac{dQ}{d\theta} = bT^4$$

where dQ is the amount of heat radiated per time $d\theta$ per unit of radiating area, T is the absolute temperature of the radiating surface, and b is a constant.

When a small body is entirely surrounded by a large one, the radiation between the two is given approximately by the formula:

$$(29) \quad \frac{dQ}{d\theta} = pc \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right]$$

where T_1 and T_2 represent the absolute temperatures of the two surfaces, c is the radiation coefficient (when English units are used $c = 0.173$ B.t.u. per hour per square foot of radiating surface of the inner body per $\left(\frac{^\circ\text{F}}{100} \right)^4$ and p is its relative blackness as compared with a perfect black body which will absorb or radiate 100 per cent of the heat passing. The approximate relative blackness of common substances is given in the following table:

Theoretical black body	1.00
Highly oxidized iron and steel	.90
Most oxides, salts, organic substances	.90
Glass	.90
Oxidized copper	.72
Aluminum paint	.50
Nickel	.35
Dull brass	.23
Polished copper	.10
Polished tin	.10
Silver (bright)	.03

Example 19. Calculate the heat delivered by direct radiation only, by a black iron steam pipe per foot of length, 3-inch outside diameter, whose surface is at 250° F. to the walls of a surrounding cylinder whose inside surface is at a temperature of 200° F.

Surface of 1 ft. of pipe 3" diameter = .785 sq. ft.

Assume $p = 0.9$, $\frac{dQ}{d\theta} = \frac{Q}{\theta}$ for steady state.

$$\frac{Q}{\theta} = 0.785 \times 0.9 \times 0.173 \left[\left(\frac{250 + 459.7}{100} \right)^4 - \left(\frac{200 + 459.7}{100} \right)^4 \right]$$

= 77 B.t.u. per hour by radiation alone. (Of course the total heat lost will be the sum of the heat of convection and the heat of radiation.)

When the body is large compared with the surroundings, the rate of heat flow by radiation is calculated from the following equation:

$$(30) \quad \frac{dQ}{d\theta} = \frac{\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4}{\frac{1}{p_1 c} + \frac{1}{p_2 c} - \frac{1}{c}}$$

when p_1 and p_2 are the relative radiation coefficients of the two bodies.

Example 20. A certain fabric is dried by passing it horizontally over rollers underneath a bank of steam pipes. If the outside of the steam pipes is at a temperature of 300° F. and the surface of the fabric is at 100° F., calculate the rate of heat radiation per square foot per hour between the two surfaces.

The preceding equation holds for two parallel surfaces of equal extent. Assume p_1 and p_2 both 0.90, and that steady state exists.

$$\frac{Q}{\theta} = \frac{\left(\frac{759.7}{100}\right)^4 - \left(\frac{559.7}{100}\right)^4}{\frac{1}{.9 \times .173} + \frac{1}{.9 \times .173} - \frac{1}{.173}} = 191. \text{ B.t.u. per hr. by direct radiation.}$$

Chapter 18

Vaporization in the Presence of Inert Gases

Heating by Gases

In the presence of inert gases, the heat of vaporization may be transmitted to the vaporizing solvent by direct contact with hot surfaces, or by radiation as before. It is more often transmitted wholly or in part by contact with the heated gas. Under these conditions the gas gives up heat to the solvent, being itself cooled in the process. This heat exchange may be considered independently of the other method of heat transmission, by radiation.

Specific Heat of Gases

The specific heat of gases at constant pressure varies with the temperature, but for most solvent recovery work large temperature changes are rarely encountered and it is usually sufficiently precise to consider the specific heat a constant for any particular gas.

For diatomic gases such as H_2 , O_2 , N_2 , CO , NO , HCl , HBr , as well as for dry air, the molal heat capacity may be expressed by the formula:

$$(31) \qquad 6.5 + 0.0010T$$

where T is the temperature of the gas in degrees centigrade, absolute. Thus the specific heat of oxygen (molecular weight=32) at $100^\circ C$. would be:

$$\frac{6.5 + 0.0010 \times (273 + 100)}{32}$$

As stated above, such a value for the specific heat of oxygen may be used safely with small temperature

changes, but in case the change is large, its average specific heat may be calculated from the above by means of the following equation:

$$(32) \quad \text{Average specific heat} = \frac{6.5 + 0.0005 T_2}{32}$$

where T_2 and T_1 are the final and initial gas temperatures in °C., absolute.

The molal heat capacity of greater than diatomic gases is higher, but there is no simple relation. The average specific heats of some gases are given in the following table between the temperature limits stated.

Gas	Molecular weight	Temperature limits (° C.)	Specific heat
Water vapor (H_2O)	18	130 to 250	.480
Hydrogen sulphide (H_2S)	34	10 to 200	.245
Carbon dioxide (CO_2)	44	at 0	.1952
Sulphur dioxide (SO_2)	64	at 100	.2169
		10 to 200	.154
Ammonia (NH_3)	17	20 to 210	.513
Methane (CH_4)	16	100 to 200	.592
Chloroform (CHCl_3)	119.5	28 to 118	.144
Ethylene (C_2H_4)	28	10 to 200	.404
Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$)	46	110 to 220	.453
Ethyl ether [$(\text{C}_2\text{H}_5)_2\text{O}$]	74	70 to 225	.480
Benzene (C_6H_6)	78	116 to 218	.375
Methyl alcohol (CH_3OH)	32	101 to 225	.458
Acetone [$(\text{CH}_3)_2\text{CO}$]	58	129 to 233	.413

Adiabatic Heating by Gases

In the case when all the heat which is furnished for the vaporization of the solvent comes from the heat in the gas alone and from no other source, a heat balance may be written as follows:

$$(33) \quad S(T_1 - T_2) = r(H_2 - H_1)$$

This states that the drop in temperature ($T_1 - T_2$) of one unit weight of air (one pound), multiplied by its heat capacity, s , equals the increase in the solvent content of the air in pounds of solvent per pound of solvent-free air ($H_2 - H_1$) multiplied by the latent heat

of vaporization, r , of the solvent. To be exact, the heat capacity used should be that of one pound of solvent-free air plus the average heat capacity of the solvent contained in it during the course of the vaporization.

Example 21. Air at 200° F. is passed over a solid saturated with alcohol, the alcohol content of the entering and leaving air being 0.07 and 0.10 pound of alcohol per pound of alcohol-free air respectively. Calculate the drop in temperature of the air if the unvaporized alcohol remains unchanged in temperature and all the heat of vaporization comes from the heat of the air.

Latent heat of vaporization of alcohol = 372 B.t.u. per lb.
 Average specific heat of air = 0.24
 Average specific heat of alcohol vapor = .45

$$\begin{aligned} \text{Heat capacity of 1 lb. of air} + \frac{.10 + .07}{2} \text{ lb. of alcohol vapor} \\ = 0.24 + \frac{.10 + .07}{2} \times .45 = 0.28, \text{ approximately } 0.28 (200 - T_2) \\ = 372 (.10 - .07). \end{aligned}$$

$T_2 = 160^\circ \text{ F.}$, the temperature to which the air will be cooled.

The condensation of the alcohol from the air in a condenser will, of course, start only when the temperature of the air has been reduced to the dew point for the particular concentration, and condensation will continue only with further temperature lowering. The heat to be removed will be calculated in a similar manner, including the heat of cooling the air and vapor, plus the heat of condensation of that portion of the vapor condensed.

Humidity Charts for Solvents

The weight of solvent which a gas can pick up when furnishing all the heat of vaporization is very much less than that possible when the heat comes from outside sources on account of the lowering in temperature of the gas. The temperature to which a gas will drop under such circumstances depends upon the amount of solvent already present in it. Passing air through alcohol contained in a well insulated vessel should lower the temperature of both the air and alcohol until equi-

librium is reached, in the same manner as when water evaporates adiabatically into air. The mechanism by which such an evaporation will occur may be shown on a diagram similar to a humidity chart.

Figure 67 represents a modified vapor-pressure curve, AB , for alcohol, plotting the weight of alcohol associated with one pound of alcohol-free air as a function of the temperature. If air containing no alcohol and at some temperature, t_1 , is brought into contact with alcohol adiabatically, it will cool off as it picks up

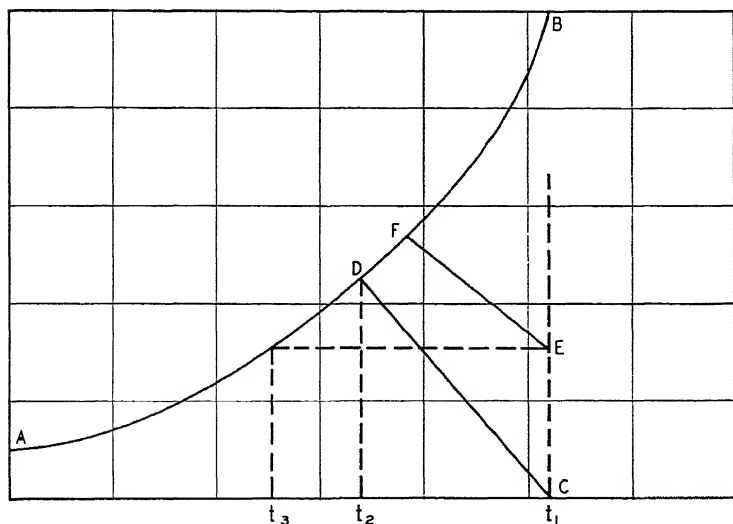


FIGURE 67.

alcohol vapor along some such line as CD , and the temperature, t_2 , corresponding to the point D , would be what might be called the alcohol wet-bulb temperature of the air under these circumstances.

If the air at the start had contained some amount of alcohol corresponding to the point E , which has an alcohol dew-point of t_3 , the cooling would have progressed along a similar line, EF , the resulting wet-bulb

temperature being higher. Such a chart may be readily constructed along the lines laid down by W. M. Grosvenor in 1908 for humidity charts in the *Transactions of the American Institute of Chemical Engineers*.

Chapter 19

The Gas Under Natural Circulation

The vaporization and condensation of solvent in the presence of air or of inert gases may occur when the air currents are due to natural convection only, or to forced convection with fans or blowers, or to a combination of the two. The simplest type of the first method is shown diagrammatically in Figure 68.

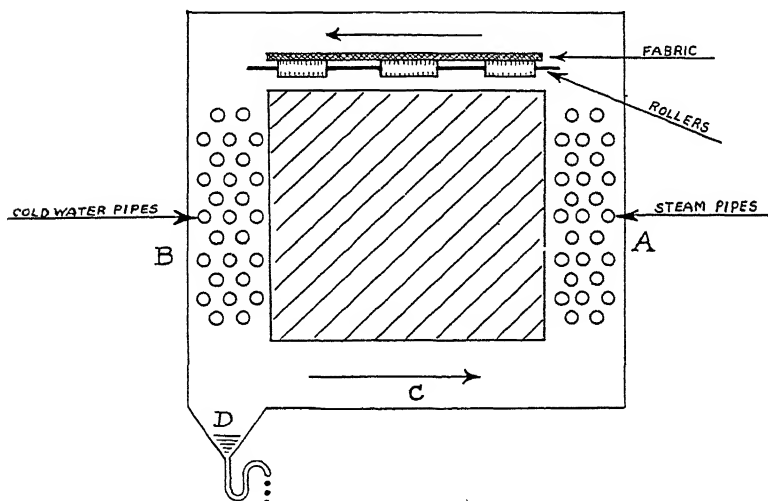


FIGURE 68. Solvent Recovery Apparatus for Natural Circulation.

This represents the end elevation of an enclosed chamber through which a fabric is passing on rollers perpendicular to the page. This chamber is connected at both sides with vertical air passages, *A* and *B*, which contain steam pipes and water pipes respectively, these passages being connected underneath as indicated at *C*.

The air heated by the steam pipes in *A* is displaced upward by the denser, cooled air in *B*, causing a counterclockwise circulation of warm air past the drying fabric, the solvent condensing from the air in *B* dripping down to a suitable receiver, *D*, as shown.

Air Velocity Due to Convection Currents

The air velocity developed in such an apparatus is low, being in the vicinity of a very few feet per second. It depends on the difference in weight between the column of heated air on one side and the column of cooled air on the other. This can be calculated from the formula:

$$\Delta P = 39.7 \left(\frac{1}{T_2} - \frac{1}{T_1} \right) h$$

where ΔP is the pressure difference in pounds per square foot, T_1 and T_2 are the average temperatures Fahrenheit, absolute, of the hot and cold columns respectively, and h is the height of the columns in feet. The rate at which the air will flow will also depend upon the frictional resistance to flow of air through the passages. This friction loss can be approximated by the method given by Wilson, McAdams, and Seltzer.¹ To this friction loss must be added the resistance due to bends, obstructions such as heating and cooling coils, and so forth.

Kent² gives the following table for the volume of air in cubic feet per minute circulated through a passage one foot square and of varying heights, the outside air being 32° F.

It is seen from this table, which makes only an empirical and constant allowance for friction and none at all for entrance and exit pressure drops, that only low gas velocities are to be expected in such types of natural draft apparatus.

¹ *J. Ind. Eng. Chem.*, **14**, 105 (1922).

² Eighth edition, p. 655.

Height of duct (feet)	Temperatures of air in duct (°F.)								
	37	42	47	52	57	62	82	132	182
10	77	108	133	153	171	188	242	342	419
15	94	133	162	188	210	230	297	419	514
20	108	153	188	217	242	265	342	484	593
25	121	171	210	242	271	297	383	541	663
30	133	188	230	265	297	325	419	593	726
35	143	203	248	286	320	351	453	640	784
40	153	217	265	306	342	375	484	683	838
45	162	230	282	325	363	398	514	723	889
50	171	242	297	342	383	419	541	760	937

Friction Loss of Air Through Heaters

The friction loss of air through heaters is not accurately known for the low velocities obtained in natural draft circulation. For higher velocities it has been determined by a number of investigators. An accurate table has been published by the B. F. Sturtevant Company for their heaters, which consist of banks of steam pipes on triangular centers. The table follows:

Friction Loss in Inches of Water at 65° F.*

Velocity of air at right angles to pipes in feet per minute, measured as though the pipes were absent	No. of rows of pipe in the heater	Pipes 1.281" outside diam. 2½" triangular centers	Pipes 1.660" outside diam. 2½" triangular centers
600	8	.06	.06
	16	.09	.09
	24	.12	.13
	32	.15	.17
800	8	.10	.10
	16	.16	.16
	24	.22	.23
	32	.27	.30
1000	8	.16	.16
	16	.25	.25
	24	.34	.36
	32	.43	.47

* Further information regarding flow of gases under natural draft may be obtained from Meier's *"Mechanics of Heating and Ventilating,"* McGraw-Hill Book Company, New York.

Inches of Water at 65° F.—(Continued)

Velocity of air at right angles to pipes in feet per minute, measured as though the pipes were absent	No. of rows of pipe in the heater	Pipes 1.281" outside diam. 2½" triangular centers	Pipes 1.660" outside diam. 2⅝" triangular centers
1200	8	.21	.23
	16	.35	.38
	24	.49	.53
	32	.63	.69
1500	8	.33	.36
	16	.55	.59
	24	.77	.83
	32	.99	1.08
1800	8	.48	.51
	16	.79	.85
	24	1.10	1.20
	32	1.42	1.55
2100	8	.65	.70
	16	1.08	1.17
	24	1.50	1.64
	32	1.94	2.11

Chapter 20

The Gas Under Forced Circulation

The use of natural draft in solvent recovery chambers is usually restricted to apparatus of small size, forced circulation being used in most large apparatus. The latter has many advantages.

Mechanism of Evaporation

The evaporation of a solvent from the surface of a solid is a complex process. The solvent which is on the surface of the solid at the start will evaporate readily enough, but that which is in the interior must diffuse to the surface before evaporation can occur, and in some cases diffusion is very slow. Furthermore, the appearance at the surface is only part of the process, for after vaporization there, the vapor must diffuse from the surface through a more or less stationary air film adhering to the surface before it meets the air flowing by and is picked up and carried away. Vaporization is therefore a process of double diffusion, and the rate at which it occurs depends upon the factors controlling these diffusions.

Suppose that the solid being freed of solvent is of the nature of blotting paper through which the liquid diffuses with great rapidity. Under these conditions the rate of evaporation is more dependent on the relatively slow diffusion through the air film than would be the case in the drying of a gelatinous material, such as Celluloid or smokeless powder, through which solvent diffuses very slowly, and under which conditions the air film is of considerably less importance.

The diffusion of the solvent vapor through this air film depends upon the temperature and corresponding

viscosities of the vapor and the air, upon the difference in partial pressure of the solvent on the two sides of the film, and upon the thickness of the film itself. Under similar conditions of temperature and partial pressure, the greater the velocity of the air over the surface, the greater the effect of tearing away the film, and the thinner the film becomes, the rate of diffusion growing correspondingly greater. This fact explains why, in the drying of textile fibers, leather-board, paper, and all other substances of that nature, through which liquids diffuse rapidly, every effort is made to give high gas velocities past the surfaces, whereas, in drying colloidal materials like smokeless powder, natural draft is often used and is very satisfactory. A very complete discussion of the rate of diffusion with respect to the evaporation of water can be found in an article by W. K. Lewis¹ and in a book by T. K. Sherwood.² wood.²

Laboratory Experiments on Rate of Drying

For data on the rate of evaporation of solvents, it is necessary to conduct laboratory experiments with respect to the material in question, as rate of evaporation can be determined in no other way. An apparatus used by the author for this purpose has been found to be very satisfactory. This is shown in Figure 69. This particular design was for the purpose of drying thin films of cellulose nitrate, rubber, and so forth, but can be readily modified to suit the material in question.

It consists of test tube *B* suspended in a glass jacket *C* through which water-vapor free air is passing in the direction shown by the arrow. The test tube is fastened by a thin wire to one arm of an analytical balance, *D*, the wire passing through a small opening in a cork in the upper end of the cylinder. At the start, the stopper

¹ W. K. Lewis, "Drying," *J. Ind. Eng. Chem.*, 1921.

² "Absorption and Extraction," New York, 1937.

in the bottom of the cylinder is removed, and the tube is lowered into a jar, *A*, containing the solution of the cellulose nitrate in the solvent, giving the film to be dried. It is then raised, the cylinder closed, and the tube weighed accurately. It is usually necessary to have the tube full of water to keep it from swinging and hitting the cylinder walls when the air is turned on. The air is then passed around the tube, being measured by a suitable meter at *F*, heated by a coil at *G*, and partially saturated with vapor of the solvent at *H*.

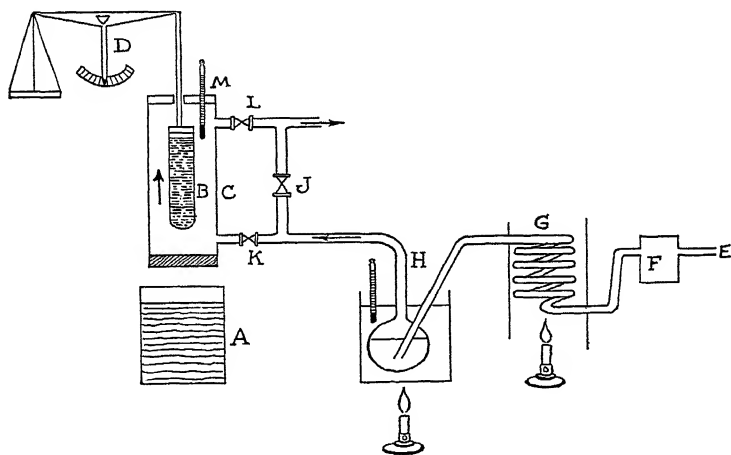


FIGURE 69. Laboratory Apparatus for Measurement of Rate of Drying of Films.

The tube is weighed at stated intervals by opening the by-pass valve, *J*, and closing *K* and *L*, which gives quiescent conditions without interfering with the air flow. The temperature is measured at *M*. The partial pressure of the vapor in the entering air is calculated by weighing the absorption bulb, *H*, before and after the run, and from the total volume of air used.

This apparatus permits the determination of accu-

rate data with varying temperature, saturation, and gas velocity, and its results can be safely used if properly interpreted in the design of plant apparatus.

Forced draft is also of great value in connection with the heating and cooling of the air, as the capacity of heaters and coolers is an important function of the gas velocity.

Flow of Heat Under Forced Draft

The rate of flow of heat between a gas and a solid surface such as the surface of a pipe has been carefully studied. At the present time the following formulas are sufficiently correct for solvent recovery problems.*

Gases Outside Pipes

Where air is flowing outside pipes and at right angles to them the Carrier formula is used. (Note: Much more exact formulas are available in other texts, but are not needed in most solvent recovery work, as other factors are usually of more importance in this particular field.)

$$(35) \quad h = \frac{22.3w}{1.42 + w} \quad \text{for 1" pipes arranged to give about 50\% minimum clear area.}$$

where h is the coefficient of heat transfer between the solid surface and the air, in B.t.u. per hour per square foot of surface exposed per degree Fahrenheit temperature difference between the solid surface and the air, and w is the mass velocity in pounds of air per second per square foot of cross-section of the heater or cooler through which the gas is flowing at the line of centers.

The total heat flowing per hour, Q , in an actual apparatus may be calculated if h is known, from the following heat flow equation.

$$(36) \quad Q = hA(\Delta t)_{\text{average}}$$

* See Walker, Lewis, McAdams and Gilliland, "Principles of Chemical Engineering," 1937.

where A is the total square feet of heating or cooling surface in the apparatus, and Δt is the average temperature difference between the walls and the air.

Example 22. A certain heater consisting of copper pipes 4 feet long, and 1 inch outside diameter and with 1 inch between pipes, arranged on triangular centers, has ten pipes in each row, and ten rows. The pipes contain steam at 10 pounds per square inch gauge pressure (24.7 pounds absolute) and the average temperature of the air passing by the pipes is 100° F. The heater is handling 4 pounds of air per second.

$$\frac{4 \times 359 \text{ cu.ft.} \times (459.7 + 100)}{29 (\text{mol. wt.}) \times (459.7 + 32)} = 56.3 \text{ cu. ft. at } 100^{\circ} \text{ F. of air per second.}$$

$$w = \frac{4.}{\frac{11 \times 1}{144} \times 4} = 13.1 \qquad h = \frac{22.3 \times 13.1}{1.42 \times 13.1} = 20.1$$

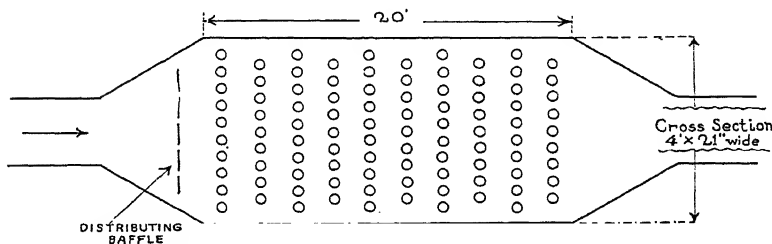


FIGURE 70. Diagram of Heater in Example 22.

The true coefficient of heat transfer between the condensing steam inside the tubes and the air outside includes the coefficients of heat flow through the metal of the pipe and from the steam to the metal on the inside; but, in the case of heating or cooling air, the resistance to flow of heat from the steam to the metal and through the metal itself is so small in comparison with that from the metal to the air that the two former are neglected, and the film coefficient figured by the Carrier equation is taken as that of the whole coefficient.

The steam pressure of 24.7 pounds absolute is equivalent to 239.4°F .

$$\Delta t = 239.4 - 100 = 139.4^{\circ}$$

$$A = 100 \text{ tubes} \times 4 \text{ ft. long} \times \frac{\pi}{12} = 104.7 \text{ square feet.}$$

Therefore $Q = 20.1 \times 104.7 \times 139.4 = 283,500$ B.t.u. per hour, which is the amount of heat delivered to the air; and since the air is flowing at the rate of 4.0 pounds per second, and since the specific heat of air is about 0.24, the rise in temperature of the air will be:

$$\frac{283,500}{4. \times 3600 \times .24} = 85^{\circ}\text{F.}$$

Gases Inside Pipes

Where gases are flowing inside of pipes, the Weber equation applies. This is:

$$(37) \quad h = \frac{0.88 \times v^{0.8} \times C_p \times T^{0.5} \times S^{0.2}}{M^{0.3}}$$

In this equation, h is the film coefficient as in the Carrier equation, in the same English units; v is the mass velocity in pounds per square foot of cross-section of pipe per second; C_p is the mean specific heat of the gas at constant pressure; T is the average temperature of the gas in $^{\circ}\text{F}$. absolute ($^{\circ}\text{F} + 459.7$); S is the reciprocal of the mean hydraulic radius in feet (in circular pipes $S = \frac{4}{d}$ where d is the inside diameter of the pipe in feet), and M is the molecular weight of the gas (air is 29).

Example 23. Carbon monoxide (CO , molecular weight = 28) is flowing through a tubular heater inside of 2" inside diameter tubes, which are ten feet long, with steam on the outside. The average temperature of the gas is 100°F . and that of the steam 239.4°F . (24.7 pounds absolute pressure). The average velocity of the gas, calculated on its volume at 100°F ., is 100 feet per second. Calculate the heat given up by each tube per hour, Q/θ , and the rise in temperature of the gas.

$Q = h A \Delta t$ (assuming that h = the overall coefficient as in the preceding example).

$$v = \frac{100 \text{ (ft/sec)} \times 28 \text{ (mol. wt.)} \times 492^\circ}{359 \text{ (\#mol. vol.)} \times (459.7 + 100)} = \frac{6.85 \text{ lbs. per square ft. per sec.}}{}$$

$$v^{0.8} = \text{antilog of } (0.8 \times \log 6.85) = 4.66$$

$$c_p = \frac{6.5 + .0010 \times 311 \text{ (}^\circ\text{C. abs. = } 100^\circ\text{ F.)}}{28} = 0.243$$

$$T^{0.5} = \sqrt{459.7 + 100} = 23.7$$

$$S^{0.2} = \left(\frac{4}{2^{1/12}}\right)^{0.2} = \text{antilog } (.02 \times \log 24) = 1.89$$

$$M^{0.3} = \text{antilog } (0.3 \times \log 28) = 2.72$$

$$h = \frac{0.88 \times 4.66 \times .243 \times 23.7 \times 1.89}{2.72} = 16.4$$

$$A = 10 \times \pi \left(\frac{1}{12}\right) = 5.23 \text{ square feet}$$

$$\Delta t = 239.4 - 100 = 139.4^\circ \text{ (as before)}$$

$$Q = 16.4 \times 5.23 \times 139.4 = 11,970 \text{ B.t.u. per tube per hour.}$$

The rise in temperature of the gas will be

$$\frac{6.85 \times \pi \left(\frac{1}{12}\right)^2 \times 3600 \times .243}{11,970} = 91.6^\circ$$

There are no data available to determine the coefficient of heat flow outside of pipes and at right angles

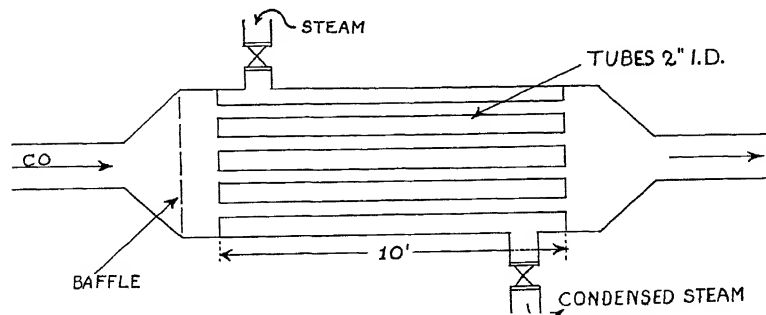


FIGURE 71. Diagram of Heater in Example 23.

to them for gases other than air. The author suggests that a good guess may be made if such a calculation is necessary, in the following manner:

- (1) Calculate h_1 for the gas inside the pipes by Weber's formula for the particular gas at the given temperature, velocity, etc.
- (2) Calculate h_2 for air inside pipes for the same conditions.
- (3) Calculate h_3 for air outside pipes by Carrier's formula for the conditions under which the gas is to flow.
- (4) Estimate the coefficient needed, h_4 , by the following ratio:

$$\frac{h_4}{h_3} = \frac{h_1}{h_2}$$

Condensing Vapor

The coefficient of heat transfer for a condensing vapor containing no non-condensable gases from the vapor to a solid condensing surface may be calculated by the McAdams and Frost formula:

$$(38) \quad h = 2200 \left(\frac{k}{z} \right)$$

where k is the thermal conductivity of the condensed vapor, and z is its viscosity relative to water at 68° F.

	Thermal conductivity of liquids (approximate)
Water	.35
Ether	.08
Acetone	.10
Methyl alcohol	.12
Ethyl alcohol	.10
Benzene	.08
Toluene	.07
Petroleum	.09
Cylinder oil	.07

Example 24.

h for condensing steam at 212° F.

$$z = .28$$

$$h = 2200 \times \frac{.35}{.28} = 2750.$$

h for condensing benzol at 176° F.

$$z = .33$$

$$h = 2200 \times \left(\frac{.50}{.33} \right) = 530.$$

h for condensing alcohol at 172° F.

$$z = .48$$

$$h = 2200 \times \left(\frac{.10}{.48} \right) = 460.$$

In the case where the condensing vapor contains non-condensable gases, the author has developed an equation which applies to condensing steam only under conditions such as are obtained in evaporators. This applies only to average percentages by volume of the steam in the steam-air mixture of from 99 to 67 per cent.

$$(39) \quad \log_{10} h = 1 + 0.0246x$$

where x is the average per cent steam.

Example 25. Steam enters a condenser containing 2 per cent of non-condensable gas, and the gas leaving the condenser contains 70 per cent water vapor. The film coefficient of heat transfer would therefore be approximately:

$$\log_{10} h = 1 + \frac{.0246(98 + 70)}{2}$$

$$h = 1160.$$

Where the condensing vapor is other than water, little is available. The author suggests in absence of better, a combination of the last equation with the McAdams and Frost formula for pure vapors.

Heat Flow to a Moving Liquid

Condensers and coolers usually have some fluid such as water separated from the condensing vapor by a dividing wall. The film coefficient of heat transfer

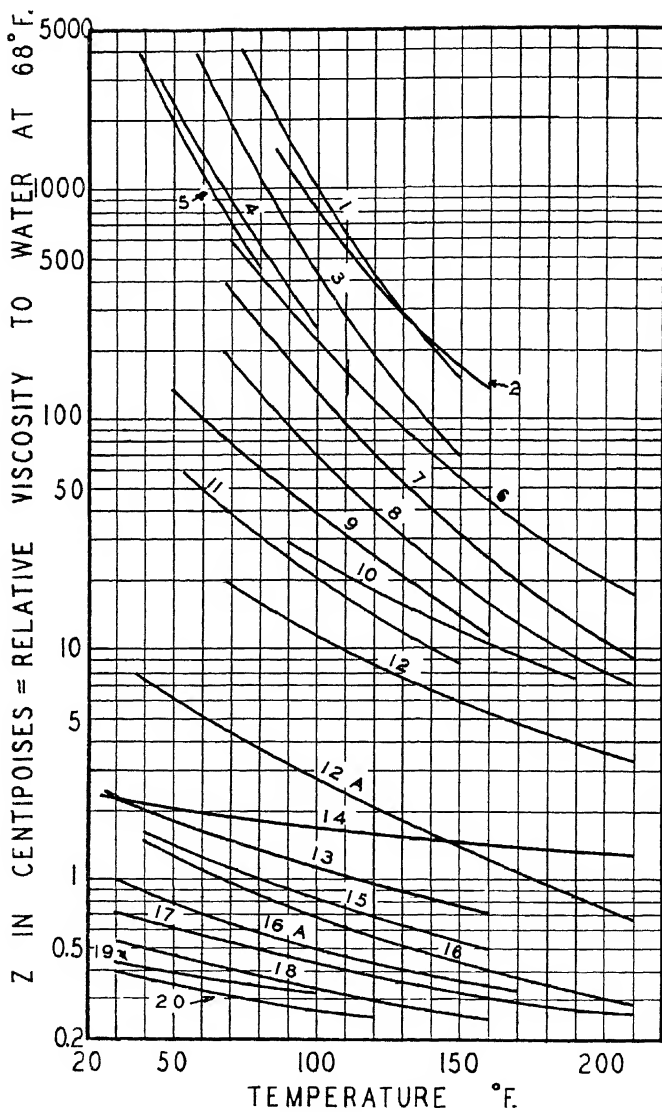


FIGURE 72.

Curve Number	Liquid
1.	Mexican crude oil
2.	Meprolene (Parks-Cramer Co.)
3.	Colorado heavy crude oil, 15.2° Be.
4.	Castor oil
5.	Glycerine
6.	Mobiloil B (Vacuum Oil Co.)
7.	Mobiloil A (Vacuum Oil Co.)
8.	Texas engine oil
9.	Olive oil
10.	Linseed oil
11.	Colorado light crude oil, 24.4° Be.
12.	Non-viscous neutral oil
12A.	Amyl alcohol
13.	Mercury
14.	Turpentine
15.	Ethyl alcohol
16.	Water
16A.	Benzene
17.	Octane
18.	Heptane
19.	Carbon disulphide
20.	Hexane

between a moving liquid and a solid surface is given by the Frost and Manley equation:

$$(40) \quad h = \frac{712cku^{0.8}s^{0.17}}{z}$$

where c is a smoothness constant, varying from 1.0 for smooth-drawn copper pipe, and 0.5 for standard steel pipe to 0.3 for dirty steel pipe; k is the thermal conductivity of the liquid as before; u is the liquid velocity in feet per second; z is the viscosity relative to water at 68° F.; and s is the reciprocal of the mean hydraulic radius in feet, as in the Weber equation above.*

Example 26. Water at 68° F. is flowing at the rate of 2.0 feet per second through a 2" inside diameter clean steel pipe. Calculate the film coefficient of heat transfer between the liquid and the wall of the pipe.

$$h = \frac{712 \times .5 \times .35 \times (2)^{0.8} (4)^{0.17}}{1.0 \times (2/12)^{0.17}} = 382$$

The overall coefficient of heat transfer between two points where there are a number of varying resistances to heat flow throughout the path of flow can be calculated only by considering the several resistances separately and then combining their effects. This is done by adding the several resistances, which are the reciprocals of the several individual conductivities, and the reciprocal of their sum will be the overall conductivity coefficient. Thus, in the case of a condenser, there is the conductivity through the metal of the tube itself and there is the film coefficient between the tube and the condenser water.

If h_v represents the vapor film coefficient, k_m the conductivity through the metal of the thickness, l , and h_L the liquid film coefficient, then U , the overall coefficient, will be calculated as follows:

$$U = \frac{1}{\frac{1}{h_v} + \frac{l}{k_m} + \frac{1}{h_L}}$$

* For a more precise formula, see "Principles of Chemical Engineering," Walker, Lewis, McAdams and Gilliland, New York, 1937.

Average Values for the Conductivity of Common Metals

Material	Temperature range (° F.)	k_m
Silver	64	243
Copper	68	238
Aluminum	32 to 212	85
Zinc	64	64
Brass	32 to 212	55
Iron (wrought)	32 to 527	40
Iron (cast) 3.5% C	86	36
Tin	32	35
Steel	82	32
Nickel	68 to 392	32
Lead	59	20

k_m is expressed in B.t.u. per square foot of surface per ° F. temperature difference for one foot of thickness of metal.

Values for other solids may be found in any handbook of chemical or mechanical engineering.

Where the solid wall consists of more than one layer of different metals, the individual resistances are added in place of the one resistance as given.

Example 27. A condenser receives steam at 212° F. and is cooled by water under the conditions stated in Example 26 on page 185 where the film coefficient on the water side was calculated to be 382. That on the steam side was found, on page 183, to be 2750. If the steel tube were $\frac{1}{8}$ inch thick, l/k_m for the metal would be

$$\frac{\frac{1}{8} \times 12}{32} = \frac{1}{3070}$$

If the condenser had been in the form of a flat plate, the value of U would then have been figured by means of equation 41, or

$$U = \frac{1}{\frac{1}{2750} + \frac{1}{3070} + \frac{1}{382}} = 302.$$

But since the condenser consists of a tube, the inside area of which is less than the outside, and for each unit length (foot) of tube the actual areas should be used, and U' (the overall coefficient per foot of tube) calculated as follows:

The inside area of one foot of 2" inside diameter pipe is

$$\frac{2\pi}{12} = 0.523 \text{ sq. ft.}$$

The outside area (diameter = 2.25") is

$$\frac{2.25\pi}{12} = 0.589 \text{ sq. ft.}$$

The average area of the metal in the pipe is really the logarithmic mean of the inside and outside areas, but for thin-walled pipes the arithmetic mean is sufficiently precise, and is

$$\frac{0.523 + 0.589}{2} = 0.556 \text{ sq. ft.}$$

To calculate U' , proceed as follows:

$$U' = \frac{1}{\frac{1}{2750 \times .589} + \frac{1}{3070 \times .556} + \frac{1}{382 \times .523}} = 161.$$

To compare U as figured for a flat plate and U' , the latter must be divided by the average area of the pipe per foot of length, or .556 sq. ft.

$$\frac{161}{.556} = 290$$

as compared with 302 for the flat plate. This deviation becomes more marked as the ratio of thickness of the metal to the diameter of the pipe increases.

Drop in Pressure Through Coolers

The factor next in importance to the coefficient of heat transfer in the design of condensers is the drop in pressure of the fluids passing through them. In general, it may be stated that the more rapid the flow of fluid the greater the coefficient of heat transfer and the greater the drop in pressure. The design of condensers therefore becomes an economic balance between the saving in heating surface and the increased cost of pumping the gas or liquid.

The drop in pressure experienced when a fluid passes through an apparatus is due to a combination of several effects of which the principal ones are friction and change of velocity. The change in potential head due to a change in the height of the fluid above some fixed level must also be considered.

Contraction Losses

When the passage through which the fluid passes has cross-sections of varying area, causing increases or decreases in the fluid velocity, the pressure drops experienced at such points are known as contraction and expansion losses respectively. The loss in pressure

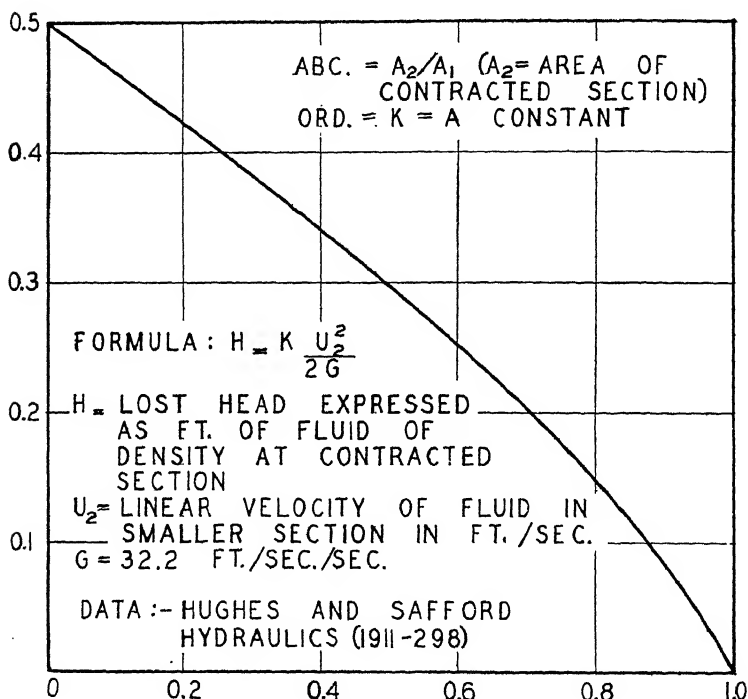


FIGURE 73.

expressed as equivalent feet of head for sudden contraction losses is given by the equation:

$$(42) \quad \Delta p = \frac{ku^2}{2g}$$

where u is the linear velocity of the fluid in the smaller

cross-section, g is 32.2, and k is a constant to be determined from the diagram in Figure 73.

Example 28. Water is flowing through a pipe 4" in diameter which is reduced suddenly to 2" diameter. The velocity in the 2" pipe is 4 ft. per second.

$$\Delta p = \frac{k(4)^2}{64.4}, k \text{ from the diagram is found for}$$

$$\frac{A_2}{A_1} = .25 \text{ to be } 0.405.$$

$$\Delta p = .062 \text{ ft. of water pressure drop.}$$

Enlargement losses may be determined from the formula

$$(43) \quad \Delta p = \frac{(u_1 - u_2)^2}{2g}$$

Thus the water issuing from the 2" pipe as above into a 4" pipe would suffer a pressure drop of

$$\frac{(4 - 1)^2}{2g} = .144 \text{ ft.}$$

For flow of compressible fluids such as air or vapor where the pressure drop is considerable (more than 10 per cent of the absolute pressure on the fluid), the reader is referred to Marks, "*Mechanical Engineer's Handbook*" or any book on thermodynamics.

Pressure Drop in Circular Pipes

The pressure drop for fluids flowing in circular pipes is calculated from the Fanning formula:

$$(44) \quad \Delta p = \frac{2 f N \rho u^2}{g d}$$

where N is the length of the pipe in feet plus the equivalent length of elbows and other constructions, and ρ is the density of the liquid.

Equivalent lengths, expressed as diameters of additional lengths of pipe (Walker, Lewis and McAdams).

90° elbows	1" to 2½"	30 diameters
	3 to 6	40 diameters
	7 to 10	50 diameters
Tees	1 to 4	60 diameters
Crosses		50 diameters
Globe valves	1 to 2½	45 diameters
	3 to 6	60 diameters
	7 to 10	75 diameters

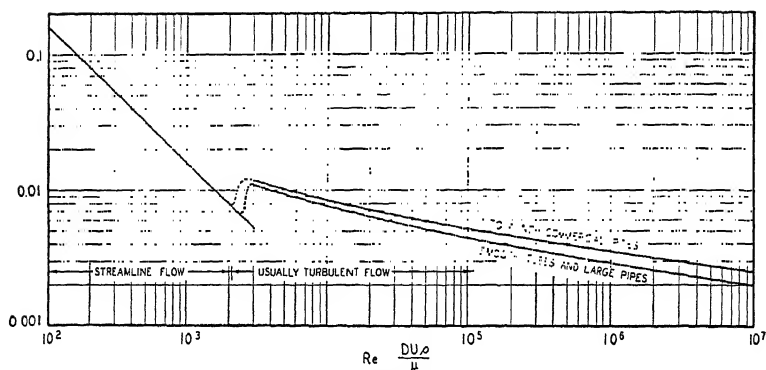
ρ = the weight in pounds of one cubic foot of the fluid.

u = the average velocity of the fluid in feet per second.

$g = 32.2$.

Δp = pressure drop in pounds per square foot.

f = the friction factor to be determined from Figure 74.



From Weber "Thermodynamics for Chemical Engineers"
(John Wiley & Sons, Inc.)

FIGURE 74.

in which f is plotted against $\frac{du\rho}{z}$ where

d = the inside diameter of the pipe in feet,

ρ = the density of the liquid, in pounds per cubic foot,

z = its viscosity, in centipoises multiplied by 0.000672.

(See Figure 72.)

Example 29. Calculate the drop in pressure of water at 68° F. flowing through 1000 feet of 3" pipes at a velocity of 2 feet per second.

$$\frac{du\rho}{z} = \frac{3 \times 2 \times 62.4}{12 \times .000672} = 46,500 \text{ and therefore } f = .0061 \text{ from the diagram.}$$

$$\Delta p = \frac{2 \times .0061 \times 1000 \times 62.4 \times (2)^2}{32.2 \times 3/12} = 378 \text{ lbs. per sq. ft.} \\ = 2.63/\text{lbs./sq. in.}$$

For pipe sections other than circular, such as the annular space in a double pipe cooler, it is suggested that in place of d in the Fanning formula, $4m$ be substituted where m is the hydraulic radius in feet (the area in square feet divided by the perimeter in feet), and that the same thing be done in determining f . For very low velocities in non-circular passages, the friction may be much higher than this calculation would indicate (due to non-turbulent flow).

For pressure drop for air at right angles to the outside of pipes, see page 178.

Chapter 21

Apparatus Used in Forced Circulation of Gases

The principles involved in the vaporization and condensation of solvents in the presence of gases are the same whether the gas is inert and non-condensable in the usual sense of the word, or if it is superheated vapor of the solvent in question. While it is possible to use the inert gas only once, discarding it after leav-

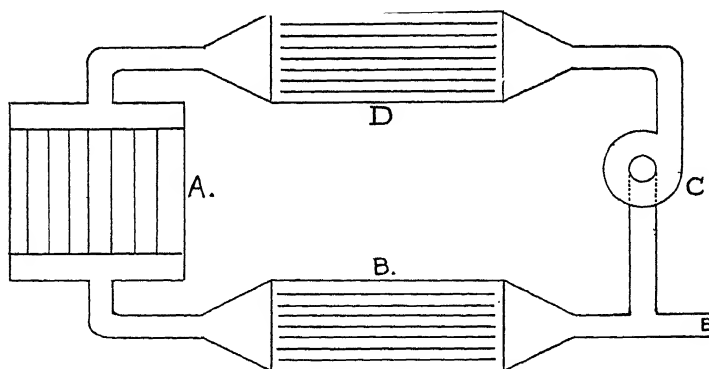


FIGURE 75. Diagram of Gas Circulation System.

ing the condenser, and heating fresh gas in the condensation method of solvent recovery, this is not often done except in special cases. It is usually returned to the system after partial removal of the solvent. A diagrammatic representation of the usual type of plant is given in Figure 75.

This consists of a drier, *A*, in which the solvent is

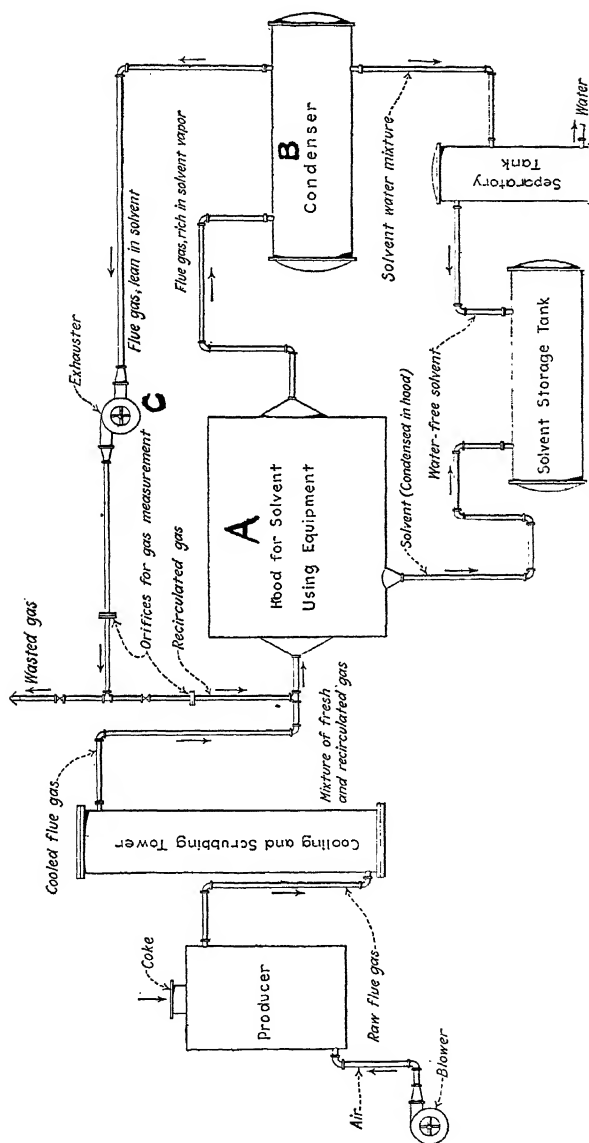


FIGURE 76. Example of System Using Gas Circulation.

vaporized, the condenser, *B*, in which part of the solvent is condensed and removed from the system, the blower, *C*, and the preheater, *D*. Fresh gas enters at *E* to replace what is lost in leaks in the rest of the apparatus. Once the apparatus is in operation, the fresh gas entering is usually negligible as compared with the volume circulated.

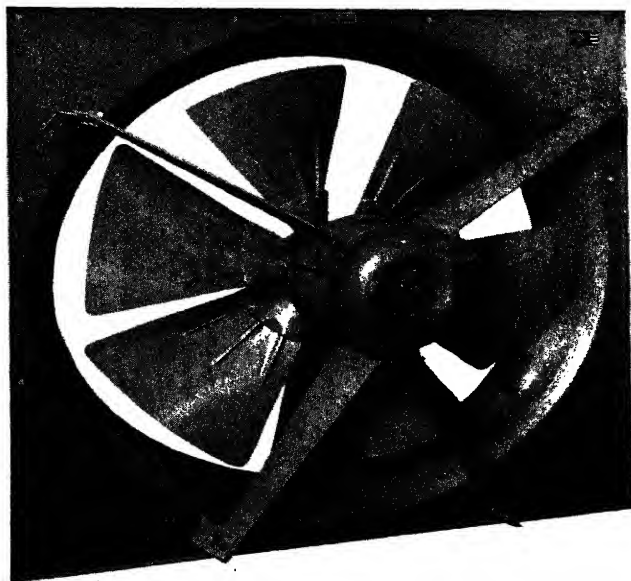
A well worked out design for a plant making use of this method of recovery by the Lewis process is given in the diagram in Figure 76.¹ In this diagram the drier is indicated by the letter *A*, the cooler by *B*, and the blower by *C*, as in the previous figure. In this case, however, the heat for vaporizing the solvent is furnished by steam pipes inside of the drier itself, instead of by a preheater as before. In many cases a combination of the two methods is used. In the present case, the gas used as a circulating medium is a washed producer gas, produced as indicated in the diagram, in order to avoid the formation of an explosive mixture. The separator tank is for the purpose of removing from the condensed solvent by decantation any water which may have been condensed in the cooler along with it.

Fans and Blowers

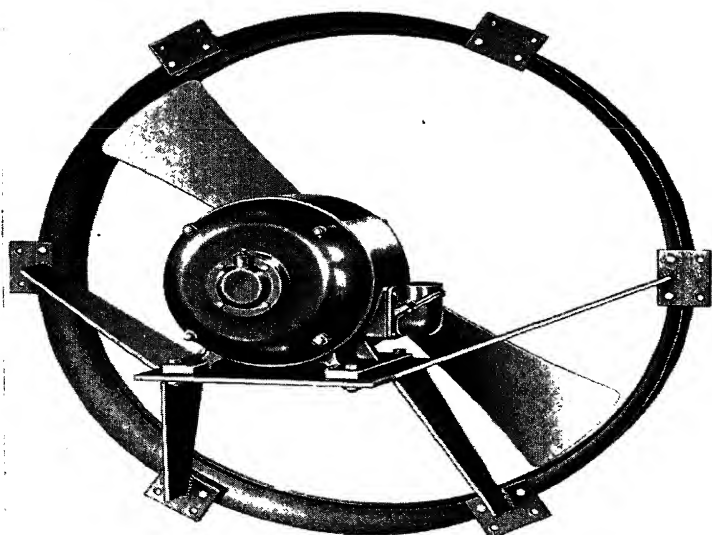
The use of forced circulation in solvent recovery requires suitable blowers or fans. Any of the well known makes are suitable, the chief thing necessary to consider being the pressure drop against which the fan must operate.

For handling large amounts of gases under very low pressure drops, below one inch of water, the type of fan shown in Figures 77, 78, and 79 is suitable (propeller type). This type of fan is very rarely used, however, as pressure drops of such small amounts are not common in solvent recovery work.

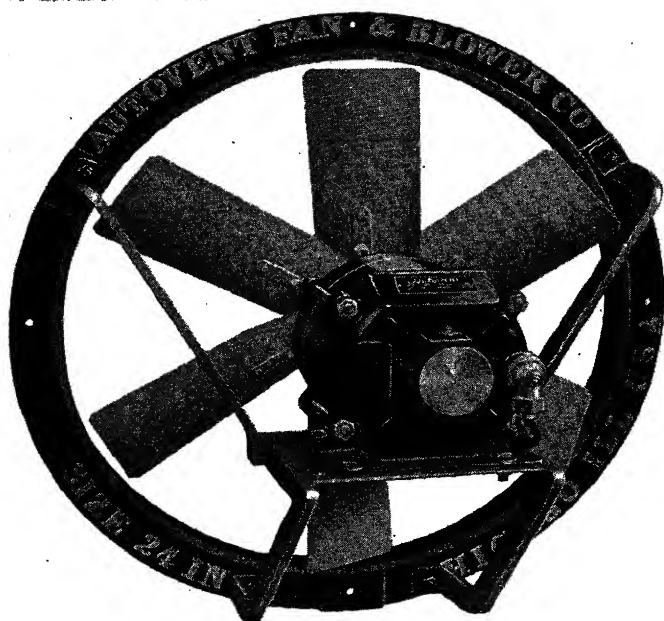
¹From B. F. Dodge, "Explosion-proof Process of Solvent Recovery," *Chem. Met. Eng.*, 26 (1922).



Courtesy B. F. Sturtevant Co.
FIGURE 77. Propeller Fan.



Courtesy Propellair, Inc.
FIGURE 78. "Propellair" Fan.



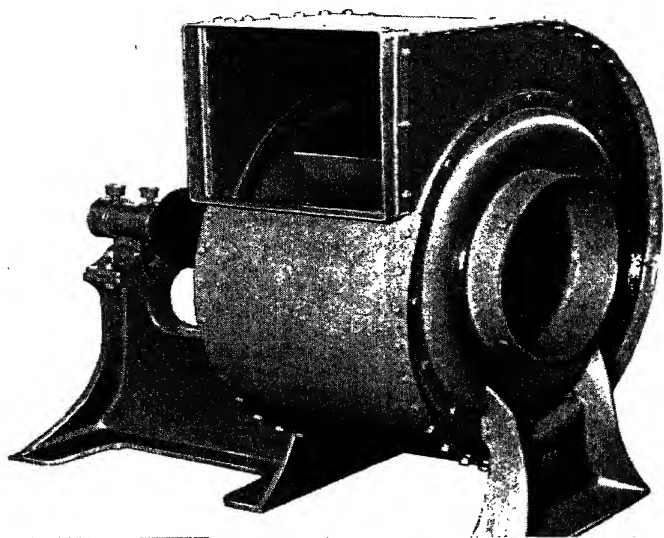
Courtesy Autovent Fan and Blower Co.

FIGURE 79. Vapor Explosion-proof Propeller Fan.

For any volume of gas up to a maximum pressure drop of 8" of water fans similar to Figure 80 are available (multi-vane type).

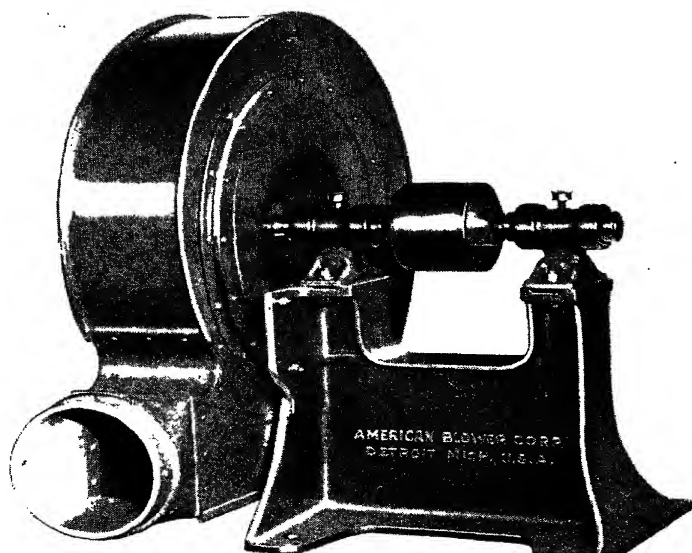
For pressure drops up to 15 inches and for any volume, fans of the Steel Plate or Planing Mill Exhaustion types are suitable, as illustrated in Figure 81.

For volumes at pressures from 18 inches to 10 pounds G or higher, turbo-blowers or positive pressure blowers may be used. Figure 82 shows a typical single-stage turbo-blower, good for pressures up to 6.25 pounds G and Figure 83 shows a multistage turbo-blower, which can be used up to about 30 pounds G. Figures 84 and 85 show the construction of a Roots-Connersville positive pressure blower.



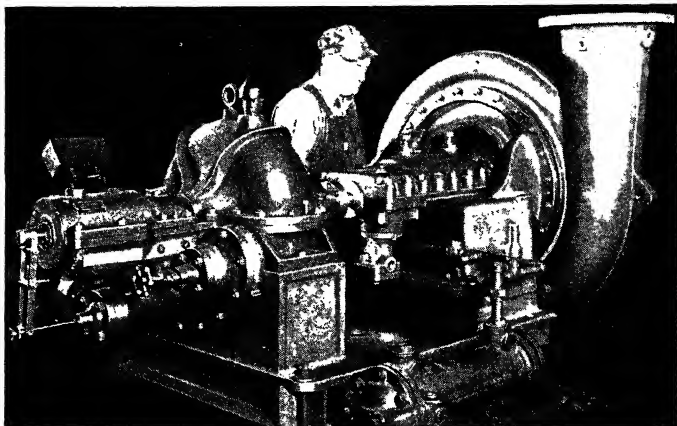
Courtesy American Blower Corp.

FIGURE 80. Multivane Type Fan.



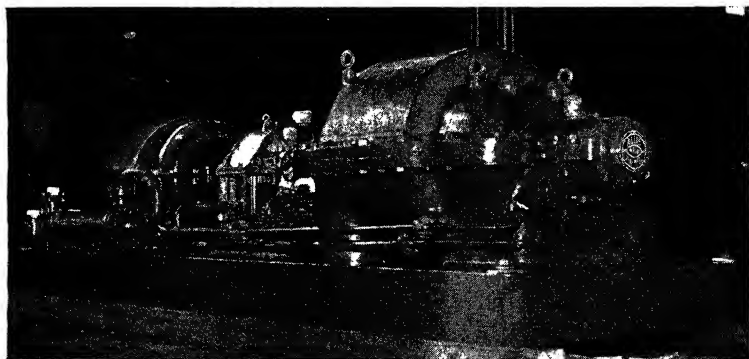
Courtesy American Blower Corp.

FIGURE 81. Steel Plate Fan.



Courtesy Allis-Chalmers Mfg. Co.

FIGURE 82. Pedestal type Single-stage Turbo-blower driven by Non-condensing Steam Engine.



Courtesy Allis-Chalmers Mfg. Co.

FIGURE 83. Multi-stage Turbo-blower, 6660 RPM, driven through gears by 300 Hp. motor.

These blowers are available for any amount of gas up to pressures of 10 pounds per square inch.

For pressure drops of still greater magnitude, compressors of the reciprocating type are required.

The actual power consumption of the fan is the theoretical power consumption of the fan divided by

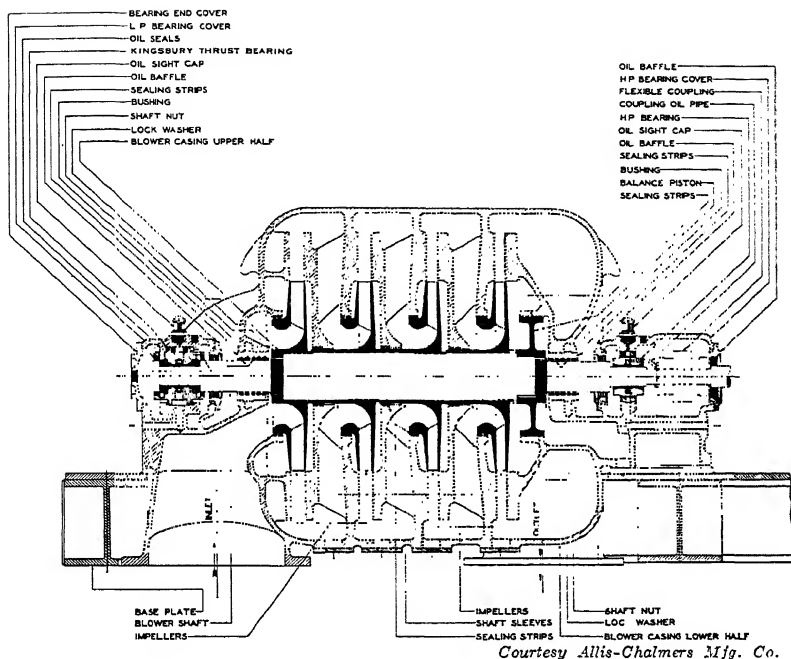


FIGURE 83a. Cross-section of Multi-stage Turbo-blower.

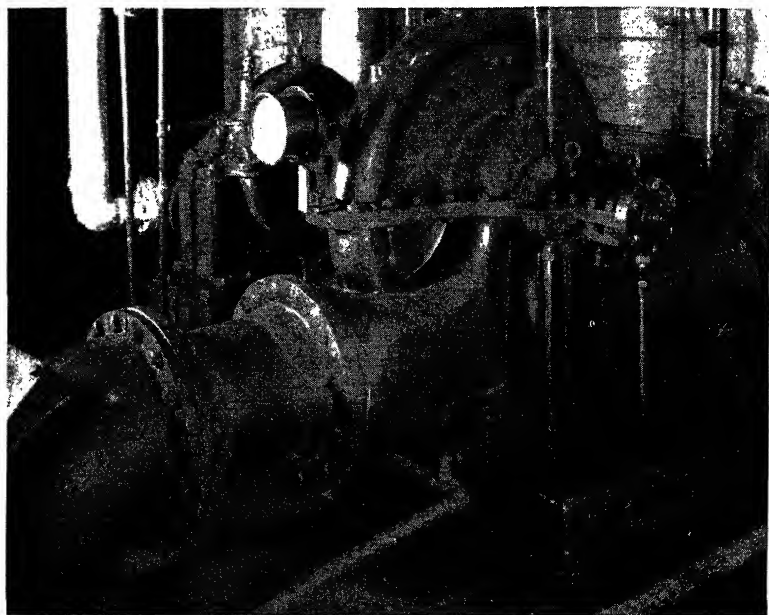
The unit shown above has four stages (impellers in series). The same general construction is followed with units having two, three, five or six stages. End seals are of the labyrinth type. Impellers are of the shrouded backward-bladed type. Thrust is balanced by a balance piston, supplemented by a Kingsbury thrust bearing. Unit illustrated has openings directed vertically downward and is driven from discharge end.

the efficiency. The fan efficiency depends upon the conditions under which it operates, but where a suitable fan is chosen, the efficiency may be taken as from 40 to 50 per cent.

Example 30. The theoretical power required to blow 10,000 cubic feet of air at 32° F. and normal barometer (29.92 inches of mercury) per minute against a back-pressure of 6 inches of water, is calculated as follows:

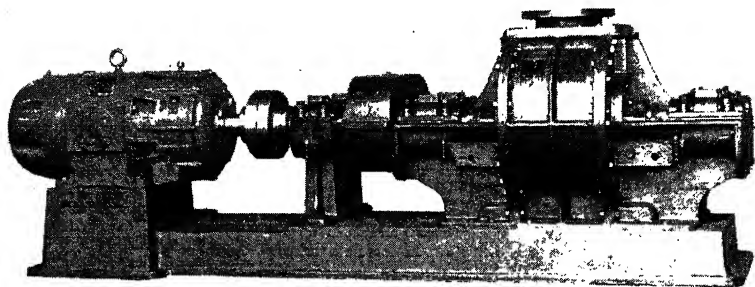
$$\text{Work } (W) = NRT \log \frac{p_2}{p_1}$$

for perfect gases (and approximately for ordinary gases) at constant temperature, where



Courtesy Roots-Connersville Blower Corp.

FIGURE 84. Gas Booster or Blower.



Courtesy Roots-Connersville Blower Corp.

FIGURE 85. Pressure Blower.

A.B.K

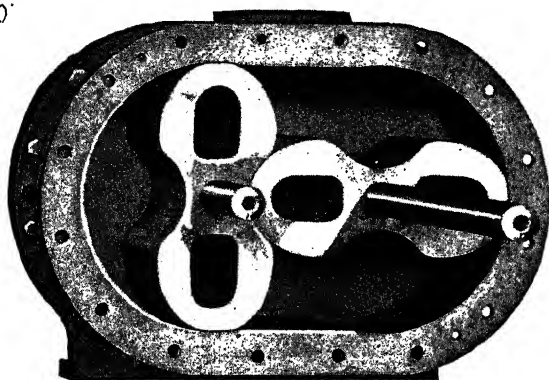
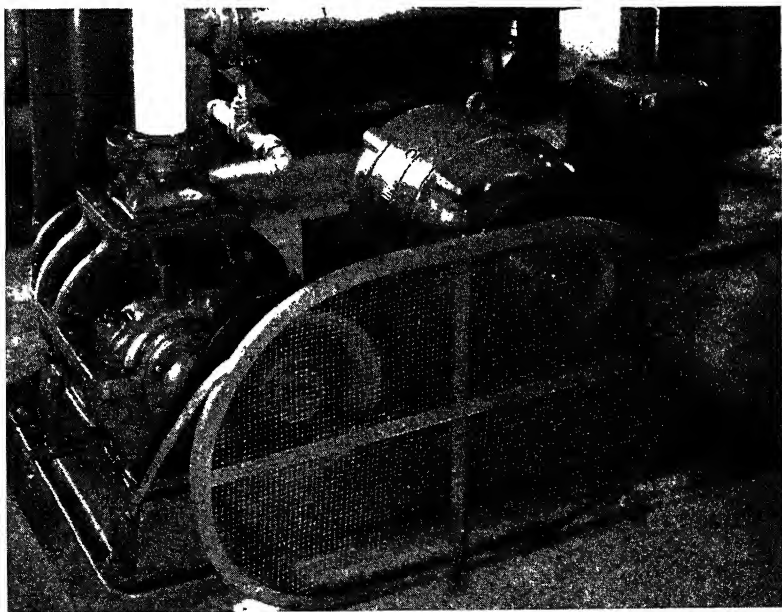


FIGURE 86.

High-Pressure
Rotary Blower
(Sectional
view).



Courtesy Roots-Connersville Blower Corp.

FIGURE 87. High-pressure Rotary Blower.

N = number of molecular weights of gas handled.

R = the gas constant (1546).

T = the absolute temperature (in this case taken as °F. abs.).

$$= 27.8 \text{ mols.}$$

$T = 492^\circ \text{ F. abs.}$

Specific gravity of mercury = 13.6.

$$W = 27.8 \times 1546 \times 492 \times \log_e \frac{29.92 + \frac{6}{13.6}}{29.92} = 317,000 \text{ ft.-lbs./min.}$$

$$\text{Horsepower} = \frac{317,000}{33,000} = 9.3.$$

If the efficiency of the blower is taken as 40%, the actual power required will be

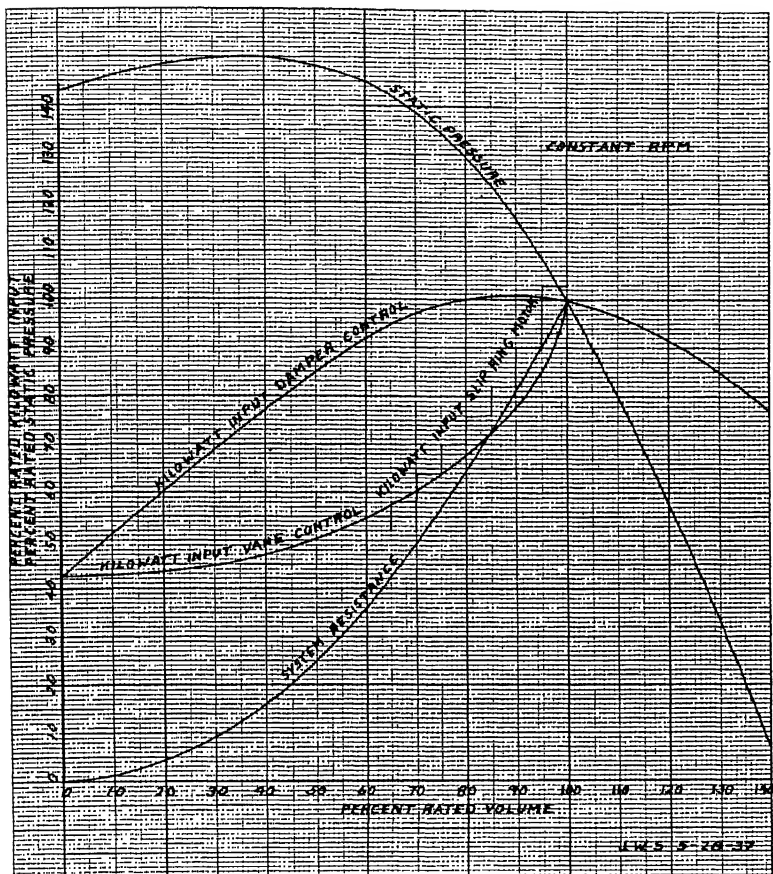
$$\frac{9.3}{.40} = 23.3 \text{ horsepower.}$$

Control of Air Flow

In the handling of vapor-laden air the matter of explosion hazards is of paramount importance. The quantity of air aspirated from the point of vaporization will control the concentration of vapor in the mixture. It is advantageous to maintain the vapor concentration at the lowest limit commensurate with proper recovery yields, and to this end control of air flow is of utmost importance.

Prior to 1925 there were two commonly accepted methods of controlling the volume and pressure established by a fan. The first may be termed the Outlet Damper Method, making use of a constant-speed motor with the output of the fan controlled by a damper in the outlet. The second may be called the Variable Speed Method, in which a variable-speed motor is used to control the output of the fan.

According to the first method the efficiency of the fan changes at every point of setting of the outlet damper. The control is spotty and the process wasteful. With the variable-speed method the motor effi-



Courtesy B. F. Sturtevant Co.

FIGURE 88. Comparison of Control Methods.

ciency is reduced and the operating cost correspondingly increases. It has the further disadvantage that the range of adjustability is narrow and limited.

In order to overcome these disadvantages and difficulties, B. F. Sturtevant Company developed some years ago a so-called Vane Control which has the advantages, but not the drawbacks, of the previously mentioned methods. With this method of control, the

fan is driven at constant speed with a constant-speed motor, but both the volume and pressure of the fan are controlled either manually or automatically by a series of movable vanes located at the inlet. The entering air is directed toward the wheel with different velocities of spin in the direction of rotation of the wheel, thus reducing the amount of work to be done on the air by the fan to meet the requirements of the system. The input of the motor varies exactly as the work done by the fan. As shown by Figure 88, this system affords great savings in power, to which should be added the advantages of uniformity of operation and possibility of automatic control.

Chapter 22

Solvent Recovery by Compression and Cooling

Work of Compression. Perfect Gases

The compression of a perfect gas from the pressure p_1 to some other pressure p_2 at constant temperature T requires an amount of work, W , as indicated by the following equation:

$$(45) \quad W = RT \log_e \frac{p_2}{p_1} \text{ (for frictionless compression only)}$$

for one mol of a gas where R is the gas constant, 1.99, when measured in heat units.

When the compression is frictionless and adiabatic, that is, when no heat enters or leaves the system, the work required to compress one mol of the gas is given as follows:

$$(46) \quad W = \frac{p_1 v_1 - p_2 v_2}{k - 1}$$

where k is the ratio of the specific heat of the gas at constant pressure to that at constant volume, being 1.4 for diatomic gases such as oxygen and air; v represents the volume of the gas in proper units, such as cubic feet. Both of these formulas neglect friction.

Actual Gases

The relation between the pressure and the volume of a perfect gas at constant temperature is given by the equation

$$(47) \quad pv = \text{constant}$$

For perfect gases this relation is given as follows:

$$(48) \quad pv^n = \text{constant}$$

the value of n being equal to 1 for isothermal compression. For frictionless adiabatic changes the value of n is equal to k , and in case of air in the ordinary cases of air compression, n is approximately equal to 1.3.

For gaseous mixtures k is estimated as follows:
 $k = \frac{\text{Average } C_p}{\text{Average } C_v}$ where weighted averages of the gaseous mixture are used.

The temperature obtained after an adiabatic compression or expansion is calculated as follows:

$$(49) \quad \frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}}$$

and the work done on the gas during the compression is calculated by the equation:

$$(50) \quad W = \frac{k(p_2v_2 - p_1v_1)}{k - 1}$$

Example 31. One mol, 29 pounds, of air is compressed adiabatically in a compressor without a water jacket to remove the heat, from one atmosphere to five atmospheres pressure, the initial pressure being 70° F. Calculate the theoretical, frictionless work needed to do this and the temperature of the air after the compression. (The actual work needed will, of course, be the theoretical work divided by the efficiency of the compressor.)

Assume that the value of n in this case is 1.3.

$$v_1 = 359 \times \frac{459.7 + 70}{459.7 + 32} = 387 \text{ cu}$$

$$= p_2v_2^{1.3}, \quad v_2 = 111. \text{ cubic feet.}$$

$$W = \frac{1.3 (5 \times 111 - 1 \times 387)}{1.3 - 1} = 730 \text{ foot-atmospheres or}$$

$$730 \times 14.7 \times 144 = 1,546,000 \text{ foot-pounds.}$$

If this amount of air were to be compressed in the time of one minute, there would be required an amount of power equal to

$$\frac{1,546,000}{33,000} = 47 \text{ horsepower.}$$

The temperature of the air after the compression would be calculated as follows:

$$\frac{T_2}{530} = \left(\frac{5}{1}\right)^{\frac{0.3}{1.3}}, T_2 = 769^\circ \text{ F. abs.} = 309^\circ \text{ F.}$$

The theoretical work that a gas will do when it expands adiabatically doing work in a cylinder is exactly the equivalent of the work required to compress it between the same pressure limits. The actual work that it will do in this case is, however, the theoretical work multiplied by the efficiency of the expansion engine. The temperature that will be reached in such an expansion will be the theoretical temperature corrected for the heat developed in the cylinder by friction.

It is better not to attempt to cool the gas by expansion through a throttling valve as is done in the case of condensable vapors below their critical temperatures, as the cooling obtained this way, known as the Joule-Thomson effect, is relatively small compared with that obtained by expansion in a cylinder doing work.

Vapors

Gases that exist below their critical temperatures are ordinarily called vapors, as it is possible to cause them to condense if the pressure on them is sufficiently raised. Most of the vapors that one has to do with in solvent recovery work are substances that are liquid at ordinary temperatures and at atmospheric pressure. And it is only by raising their temperature or lowering the pressure at which they are present that they may be obtained in the gaseous condition.

A vapor that consists of only one substance may exist in either the saturated or the superheated condition. When it is in the former, its pressure corresponds to a definite temperature, whereas when it is in the superheated condition its pressure and temperature may be varied independently of each other.

When a pure vapor is in the saturated condition, some of the same substance in the liquid condition can be introduced into it, if at the same temperature, without changing the pressure or temperature. When this happens, the vapor is in the wet or moist condition, and heat can be applied to the mixture of vapor and liquid without any other effect than vaporizing some of the liquid at constant temperature and pressure. When enough heat has been supplied to vaporize all

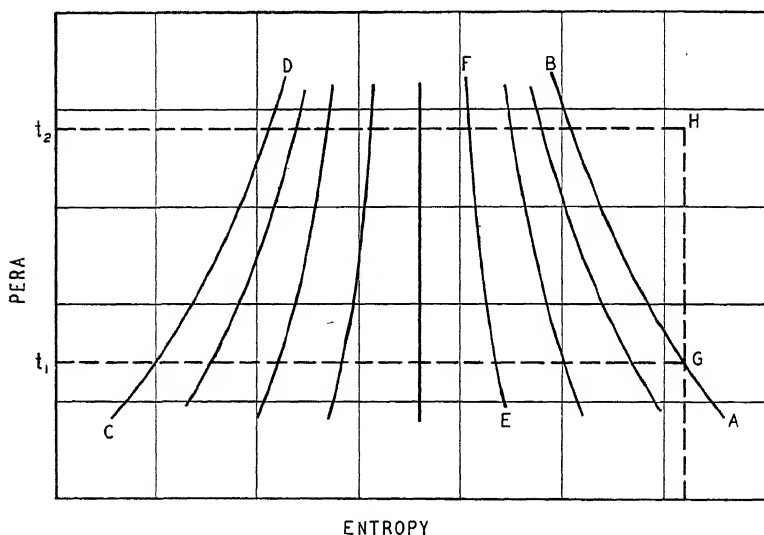


FIGURE 89.

the liquid present, any further application of heat will cause the temperature to rise and the vapor will become superheated.

The effect of temperature and pressure upon a pure vapor may best be shown by means of what is known as the temperature-entropy diagram, Figure 89. The term *entropy* is used to indicate a mathematical device for measuring the availability of the energy in a vapor; that is, when a vapor undergoes a change in entropy,

the energy that it contains has become more or less available according to the direction of the change.

In Figure 89, ordinates represent temperature and abscissae represent entropy. The line AB is the line for saturated steam without any liquid water, and the line CD shows the change in the temperature with the entropy for liquid water without any water vapor. The intermediate lines are for mixtures of steam and water, the line EF , for instance, representing that for a mixture of 60 per cent steam and 40 per cent water.

Suppose that the water-free or dry steam exists at the temperature t_1 , represented by the point G , and that it is compressed reversibly and adiabatically, without heat either entering or leaving the system, until it has risen to the temperature t_2 , represented by the point H . It will now be in the so-called superheated condition.

The amount of work needed to change it to this condition may be read directly from another chart, shown in Figure 90, which indicates enthalpy, or energy content in the vapor, measured in the form of heat, plotted against entropy. In this chart the line representing dry saturated vapor is shown by the line AB as in the previous chart, while the line representing a mixture of 60 per cent steam and 40 per cent water is shown by the line EF . The point G is the same as that in the previous chart, as is the point H . The lines JK , LM , etc., are lines of constant number of degrees of superheat, while those marked OP , QR , etc., are lines of constant pressure. In the chart on page 208 the number of degrees of superheat to which the vapor has been raised is represented by the distance GH or $t_2 - t_1$, and the point H on the chart on page 208 lies on the corresponding line of constant number of degrees of superheat. The increase in energy of the vapor due to this compression is indicated by the difference between i_2 and i_1 , and represents the amount of work that was done on the vapor during the compression.

When a vapor expands reversibly and adiabatically doing work in an expansion engine, the amount of work done may be determined in a similar manner. Any good book on the thermodynamics of the steam engine will give a full discussion of this subject and steam tables are available for making the necessary calculation. So far as other vapors than steam are concerned, there are available tables of properties for ammonia, sulphur dioxide, and such other substances as are used

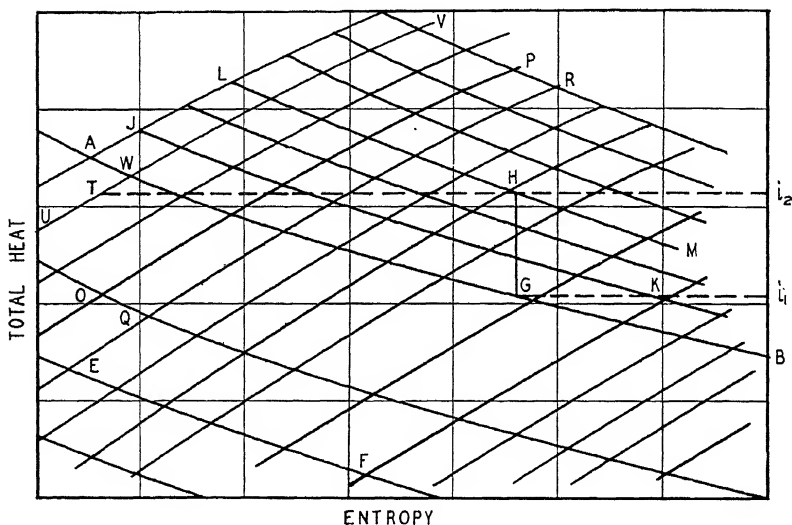


FIGURE 90.

in mechanical refrigeration, but for most of the solvents in common use, the writer knows of little available data. In the absence of such information, the most that can be done without extended investigations will be to use the steam tables as if for water, making such modifications as are necessary to allow for the variation in vapor pressure, vapor density, and specific heats of the substance in question from the corresponding values for water. Otherwise recourse must be had to a good text on thermodynamics.

Mixtures of Vapors and Gases

The problem of compressing a mixture of a vapor and a gas is almost always that of the vapor in the superheated condition, and therefore it becomes one of a mixture of two gases and can in general be solved as previously indicated. That of the expansion of a vapor or a gas is much more complicated.

The expansion of a pure vapor doing work has been indicated above. However, when the expansion takes place through an expansion valve or nozzle, it occurs practically under conditions of constant enthalpy, except as friction is developed, and the resulting condition of the vapor can be read off the enthalpy-entropy diagram, given above. For instance, suppose that the superheated vapor at the point H was allowed to expand through a throttling valve from the pressure corresponding to the point H to some lower pressure indicated by the point T ; the temperature of the gas at the end of the expansion will be that corresponding to the pressure if the line HT has crossed the saturation line AB , whereas if the point T had remained on the upper side of this line, the temperature obtained would be that corresponding to the pressure, plus the number of degrees of superheat corresponding to the location of the end of the expansion.

Advantages of Compression

The reasons for compressing a mixture of a gas and a vapor are two-fold. In the first place, the partial pressure of the vapor in the mixture is increased in proportion to the increase in the total pressure. This permits the condensation of the vapor at temperatures considerably above that at which it would condense at ordinary pressures.

For instance, suppose that a gas at atmospheric pressure is saturated with benzol vapor at 20°C. , at which temperature the vapor pressure of benzol is 74.7 mm. of mercury. If this mixture is compressed to five

atmospheres pressure, or 3800 mm. absolute pressure, the temperature being kept at 20° C. by contact with cooling surfaces in the compressor and receiver, the partial pressure of the benzol vapor would have become 5×74.7 mm. But at 20° C., the vapor pressure of benzol is 74.7 mm. Therefore, to keep this partial pressure constant, some of the benzol must have condensed. This would amount to 81½ per cent of the total, assuming the perfect gas laws to hold. The heat which must have been removed during this compression at constant temperature would have been the sum of that due to the compression of the gas, calculated as above, and that due to the condensation of the benzol at constant temperature.

The second reason for compressing the gaseous mixture is the fact that a compressed gas, when cooled, and then allowed to expand doing work, will cool itself to a low temperature, much below that which can be obtained without the use of mechanical refrigeration.

The two effects may be utilized singly or together, or, of course, in connection with any of the other types of solvent recovery.

For instance, the gas mentioned in the previous example, containing 74.7 mm. of benzol and at five atmospheres pressure, could be expanded in a cylinder or turbine doing work, and reduced to a low temperature as previously indicated, the theoretical temperature drop, neglecting the presence of the benzol vapor, being in the vicinity of 200° F. The partial pressure of the benzol in this case would therefore drop to $74.7 \div 5 = 14.9$ mm. But at -130° F. the vapor pressure of benzol is very low, being in the vicinity of 1 to 2 mm., and therefore most of the benzol in the gas would have condensed before that temperature was reached. But in condensation, the heat of condensation would have been liberated, thus decreasing the drop in temperature of the gas, the net result being a combination of the three effects, *i.e.*, the cooling due to the

expansion, the heating due to the condensation of the benzol, and the heating due to friction. It is difficult to predict the actual temperatures thus obtained, but under some circumstances, -100°F. would not be unreasonable to expect.

The final operation in a plant using this process of compression and subsequent expansion is that accomplished by the heat interchanger, the cold gas more or less freed of solvent being used to cool the hot gas

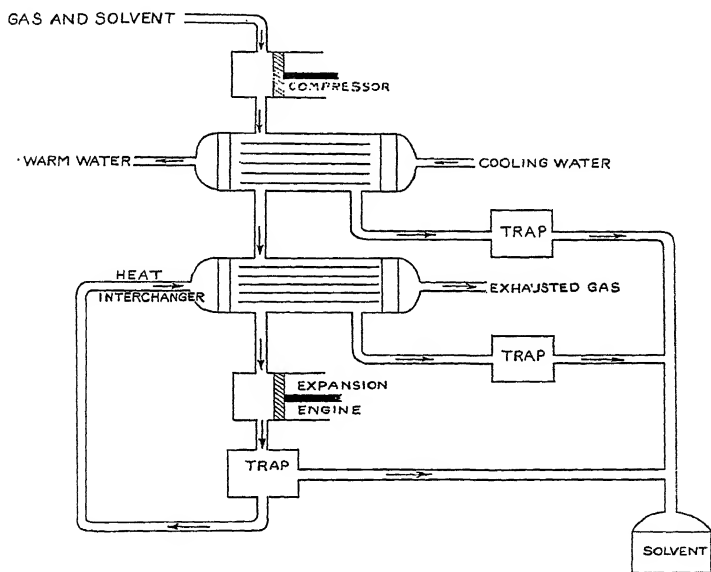


FIGURE 91. Compression System for Solvent Recovery.

leaving the compressor. The surface required in the heat interchanger may be readily estimated by the methods given above.

In general, the apparatus required for such a plant would be as indicated in Figure 91.

In this diagram the gas and vapor mixture passes successively through the compressor, water cooler, heat interchanger, expansion engine, heat interchanger, and

to the exhaust, the condensed solvent being tapped off at each point as indicated.

A plant very nearly the duplicate of this has been in operation in the writer's vicinity, the only change being the introduction of a pre-cooler for the air before entering the compressor for the purpose of removing as much heat as possible and lightening the load on the compressor. The air was then compressed in two stages with an intercooler, to 100 pounds pressure. The temperature produced after expansion, the engine doing work against friction, in the form of a band brake, produced a temperature so low that the engine and the subsequent heat interchanger were coated with ice at all times.

The chief improvement to be made in such an installation as the above would be the use of the work done in the expansion engine for the compression of the original gas, the difference being made up by additional power from an outside source. This principle of the recovery of power is the basis of the well-known Claude and the Norton processes for the liquefaction of the so-called permanent gases.

A modern plant, designed by W. K. Lewis, utilizing this principle, is shown in the accompanying diagram, Figure 92. In this, the gas is taken from a drier by the blower, and passes in succession through a forecooler, a compressor, an intercooler, an expansion engine, which assists in compressing the gas, then to a final condenser and finally to the outside air. Suitable separators and traps are indicated for removing the solvent. In this particular case the gas used is made by burning illuminating gas as shown. The drier is heated by steam coils.

In very many cases where the compression system is used, the gas is discarded after leaving the recovery apparatus instead of being recirculated, as is usually the case in the condensation system and in the scrub-

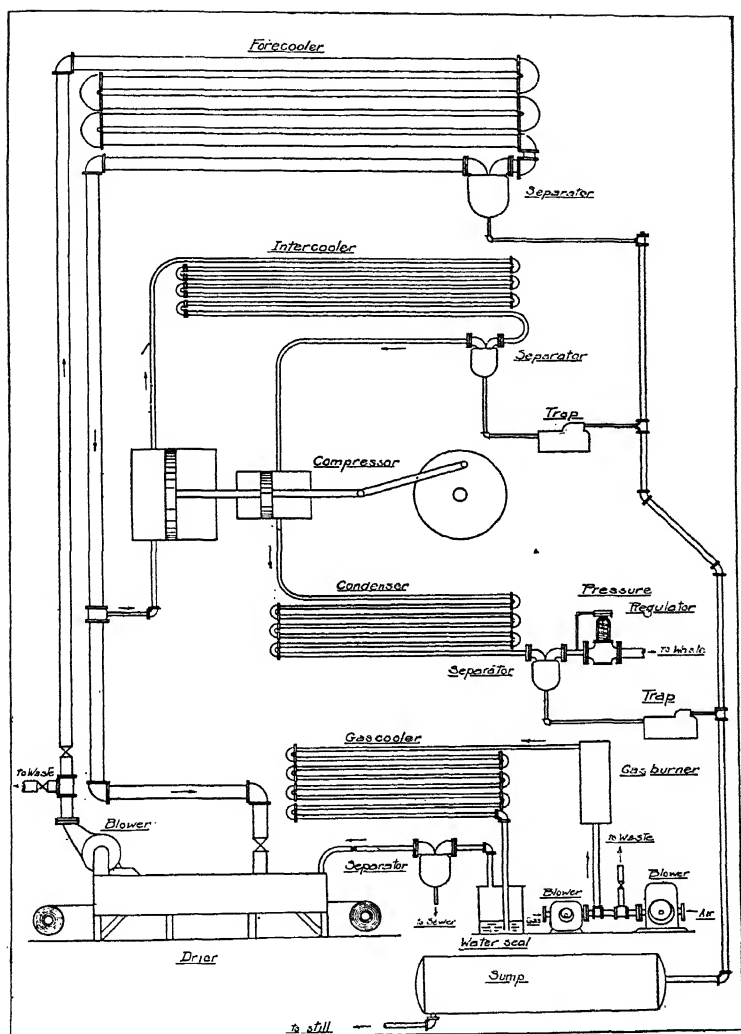
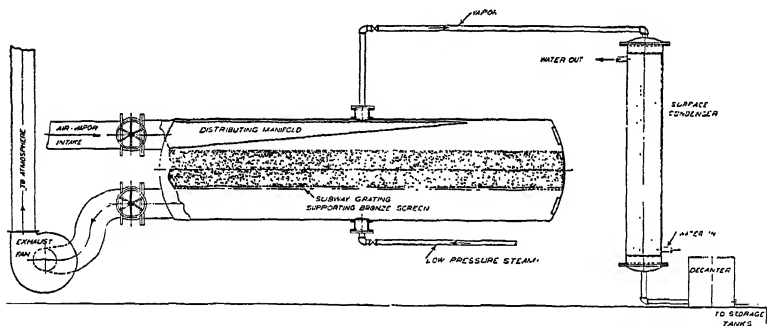


FIGURE 92. Example of Compression System.

bing system, the solvent having been so thoroughly removed from it.

In general, the compression system is most suitable for use when a relatively rich gas in small volumes must be treated and the gas is not to be recirculated. However, this method has been used for years in the recovery of gasoline from natural gas.

The problem of the design of suitable compressors, of either the reciprocating or the turbine type, and the design of expansion engines, would require more space than can be devoted to these details in this volume. The reader is referred to standard books on air compressors and to the excellent abstracts in Marks, "Mechanical Engineers' Handbook."*



Courtesy American Solvent Recovery Co.

FIGURE 93. Design of an Early Carbon Adsorption Plant.

Little difficulty is to be experienced in the compression of the gas, and standard designs for apparatus may be followed closely; but in the expansion, considerable trouble may be expected from the formation of ice, or in some cases, solidified solvent in the expansion engine. Numerous devices have been tried for overcoming this difficulty, which is especially great in the manufacture of liquid air and in other processes requiring extremely low temperatures, at which tem-

* McGraw-Hill Book Co., New York.

peratures frozen water vapor becomes for all practical purposes like so much sand, which scores the cylinders, destroys valve seats, and so forth. In such cases, the water vapor is usually removed from the gas before expansion, by means of some dehydrating agent such as silica gel, activated alumina or calcium chloride. But this is, of course, not possible in solvent recovery work, and in such cases the cylinders are often lubricated with glycerin or other oily material in which the water is soluble and which will retard the formation of crystals. Electrically heated valves have also been tried. The author is of the opinion that the expansion turbine offers the best solution of the problem, although he does not know of any use of it in solvent recovery work at the present time.

Chapter 23

Solvent Recovery by Scrubbing

Gases containing solvent vapors in small amounts can sometimes be economically treated by scrubbing with a liquid in which the vapor is soluble. This method, and the use of solid adsorbents, are the only methods available for large volumes of gas, as cooling without compression will not cause condensation in the more dilute mixtures, and compression of large volumes of gas is too expensive.

The principles involved in the solution of the vapor in the liquid are given in Chapter 4. Raoult's Law states that the partial pressure of a volatile substance over its solution in a solvent is equal to the vapor pressure of the pure substance at that temperature, multiplied by the mol fraction of the substance in the solution; and Henry's Law states that for dilute solutions, the partial pressure of the volatile substance is proportional to its mol fraction in the solution. These are indicated as follows:

$$(51) \quad \text{Raoult's Law, } p = p_0x$$

$$(52) \quad \text{Henry's Law, } p = ax$$

In the special case where $p_0 = a$, Henry's Law and Raoult's Law are identical.

The essential features of this method of solvent recovery are shown in the diagram in Figure 94.

This consists of a scrubbing tower, *A*, of some suitable construction, through which the gas containing the solvent vapor passes, entering at *B* and leaving at *C*, the scrubbing liquid entering at *D* and leaving at *E*. The scrubbing should always be counter-current, except in very special cases, as the maximum concentration of

solvent in the liquid is obtained with counter-current flow. The liquid leaving the scrubber is then subjected to a fractional distillation to remove the solvent from it and to recover it for reuse. This is done by taking the scrubber liquid through a heat interchanger, *F*, where it is heated nearly to the boiling point by counter-current indirect contact with the hot liquid discharged from the still. The heated liquid then enters the fractionating column, *G*, at the point *H*, and runs down through it into the boiling section, *M*, from

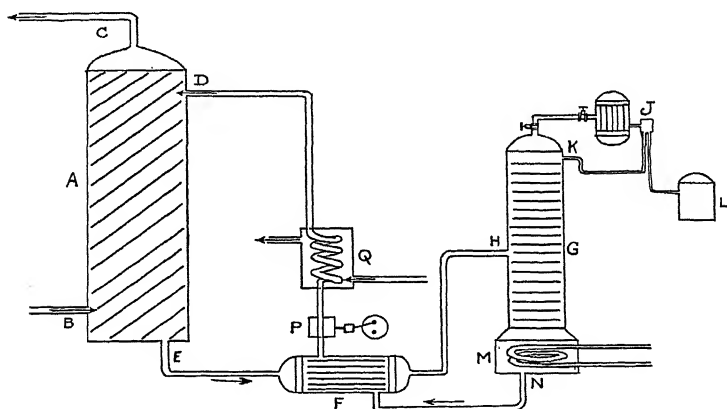


FIGURE 94. Diagram of Scrubbing System.

which it passes to heat interchanger, *F*, and then to a cooler, *Q*, being pumped from that back to the scrubbing column, *A*.

The action of the fractionating column, *G*, is as follows: the vapor generated in the section, *M*, rises through the column and causes the volatile solvent dissolved in the less volatile scrubbing liquid to vaporize, the column being so designed and the rate of boiling being so conducted that by the time the scrubbing liquid has run down through the column to the section *M*, practically all the solvent has been boiled out of it, and it is in that condition when it leaves the still at *N*.

The vapor rising through the column consists at the bottom of practically pure vaporized scrubbing liquid with very little solvent in it; but the concentration of solvent rises in the vapor as it passes up through the column, until when the vapor leaves the top of the column, it consists of practically pure solvent, if the column has been properly designed and is correctly operated. The solvent vapor is condensed in the condenser, *J*, and part of it is taken to the solvent receiving tank, *L*; the balance is allowed to run back into the top of the column at *K* and runs down through the column, washing out of the ascending vapor the vapor of the scrubbing liquid.

The design of a suitable still to be used in connection with solvent recovery equipment is a very specialized problem, and those interested are referred to the work by E. R. Gilliland and the author on that subject.¹

In any sort of operation involving scrubbing, the maximum concentration that can be obtained is that where the partial pressure of the solvent over the solution equals the partial pressure of the solvent vapor in the gas in contact with it. This can be obtained theoretically only when the time of contact between the gas and the liquid is infinitely long, in an apparatus of infinite length. Practically, this equilibrium condition can be very nearly reached in apparatus of commercial length. It usually happens, however, that it is not economical to attempt equilibrium concentration, the apparatus very commonly reaching only within 50 per cent of the equilibrium concentration. This is considered a satisfactory concentration for most work.

As stated in a previous chapter, the force that causes the solvent vapor to pass from the gas into the liquid is the difference between the vapor pressure of the solvent vapor in the gas in contact with the liquid and the partial pressure of the solvent from the liquid

¹"The Elements of Fractional Distillation," McGraw-Hill Book Co., New York, 1939.

itself, the rate at which the solvent passes from one to the other being directly proportional to this difference. This is expressed in the following equation:

$$(53) \quad \frac{dW}{d\theta} = k(P - p)$$

where dW is the amount of solvent vapor picked up by the liquid in the time $d\theta$, k is a constant depending upon conditions, P is the partial pressure of the solvent in the gas, and p is the vapor pressure of the solvent in equilibrium with the liquid.² For a very complete discussion of the theory of absorption, the reader is referred to a work by T. K. Sherwood, entitled "Absorption and Extraction."

The mechanism by which the solvent vapor passes from the gas to the liquid may best be indicated by the following method. Imagine a spherical drop of liquid in contact with gas. This drop may or may not be moving in relation to the gas in contact with it, but in either case there is around the drop and in direct contact with its surface what amounts to a stationary film of gas through which the solvent vapor must diffuse in order to get into the liquid. After coming into contact with the liquid the vapor then dissolves, forming a solution or increasing the strength of the solution already present. This forms a layer of solution on the surface of the drop, and this surface layer would soon become saturated with respect to the gas, and further solution would stop, were it not for the fact that this surface solution diffuses slowly from the surface into the interior of the drop. The whole operation of solution therefore involves the diffusion of the vapor through two distinct layers or films, and the factors governing the rate of scrubbing are largely those that affect the behavior of these films.

As has been mentioned in connection with the discussion of the flow of heat through surface films in a

² W. K. Lewis, "The Principles of Counter-Current Extraction," *J. Ind. Eng. Chem.*, 8, 827, 1916.

previous chapter, the thickness of the film is affected by a number of external factors. The greater the velocity of the gas across the surface of the liquid, the thinner the gas film and the more rapidly the solvent will diffuse through it, and therefore the more rapidly will the scrubber remove the solvent from the gas. Other factors influence the thickness of this gas film on the liquid, such as temperature, gas viscosity and the like.

The film of more or less saturated liquid on the surface of the drop is also affected by external conditions. If the liquid is in vigorous motion, the stirring action in the interior of the drop will assist materially in removing the solution from the surface to the interior. The temperature and therefore the viscosity of the liquid are also of importance in the rate of mixing.

In most types of scrubbers it is difficult to measure the area of the liquid surface exposed to the action of the gas, as the liquid is usually in more or less violent agitation and is frequently in the form of a finely divided spray. About the only type in which it is possible to get even an approximate idea of the surface of contact is in the slat type of scrubber, when there is just enough liquid running down through it to wet the surfaces of the slats. It has therefore been necessary in all other types of scrubbers to make use of an empirical measure of surface area. Suppose, for instance, that the scrubber consists of a tower down through which is falling a constant spray of liquid in the form of finely divided drops. It is assumed that so long as scrubbing conditions remain uniform, the number of drops in one cubic foot of the tower is the same as in any other cubic foot. And if the surface area of each drop averages the same, the actual total surface area per cubic foot will be the same for all parts of the column. The coefficient of diffusion in equation (53) is therefore given as per cubic foot of tower, and is called ka . And if the difference in the partial pressures

in the same equation is indicated by Δp , the equation will be written:

$$(54) \quad \frac{dW}{\tau \Delta} =$$

where V represents the volume of the tower in cubic feet.³

In all cases of the absorption of a vapor by a liquid, there is a heat effect. This is the sum of the heats of condensation and the heat of dilution of the condensed vapor in the solvent. In the case of very dilute vapors, the heat effect is usually neglected, but where the concentration of the vapor in the gas is fairly great, the heat effect is considerable and cannot be neglected except in calculations of the most approximate character. It frequently happens that the temperature of the gas and that of the liquid are different at the beginning of the absorption process. The heat of absorption tends to raise the temperature of the liquid and the gas in contact with it, and the rate of flow of heat between the two depends upon the difference in the temperatures of the liquid and the gas. The rate of heat flow is given by the same equation as that for flow through solids:

$$(55) \quad \frac{dQ}{d\theta} = h A (\Delta t)$$

In this equation the area A can be replaced by the equivalent $ha V$, where ha represents the coefficient of heat transmission per cubic foot of volume of the tower, and V represents the volume of the tower in cubic feet. The equation then becomes:

$$(56) \quad \frac{dQ}{d\theta} = ha V (\Delta t)$$

Under certain circumstances the coefficients ha and ka have definite values, namely, when the apparatus is functioning as an adiabatic humidifier with the vapor-

³ See W. G. Whitman and J. L. Keats, "Rates of Absorption and Heat Transfer between Gases and Liquids," *J. Ind. Eng. Chem.*, 14, 186 (1922).

izing liquid at constant temperature. This condition does not occur, so far as the writer knows, in any type of solvent recovery apparatus, and the actual values of ha and ka to be expected must be determined in apparatus of a nature similar to that which is going to be used in the plant, under such conditions that the values to be expected can be calculated from the experimental ones.

The coefficients of heat transfer, ha , for scrubber towers of various types are given by Whitman and Keats in Figure 95, showing the effect on this coefficient for a plate column, a coke tower, a Maclaurin scrubber, and a spray chamber.

It should be pointed out that the solid portions of the curves are experimental, while the dotted portions are extrapolated. The values given apply in equation (56) when ha is given as B.t.u. per cubic foot of tower, per hour per degree Fahrenheit difference between the liquid and the gas.

The coefficient of diffusion, ka , was determined for these towers, and the results are given in rounded off form calculated for a gas velocity of 12 pounds per square foot of cross-section of tower per minute, in the following table, where ka is pounds absorbed per cubic foot of tower per minute per millimeter vapor pressure difference between the substance dissolved in the scrubbing liquid and its partial pressure in the vapor in contact with the liquid.

	ka	Water-rate
Coke tower	.007	20
Maclaurin scrubber (centrifugal spray)	.002	100
Spray chamber (humidifier type)	.001	20
Plate column (cap style plates)	.018	20
Laboratory bubbler (perforated plates)	.045	0.5

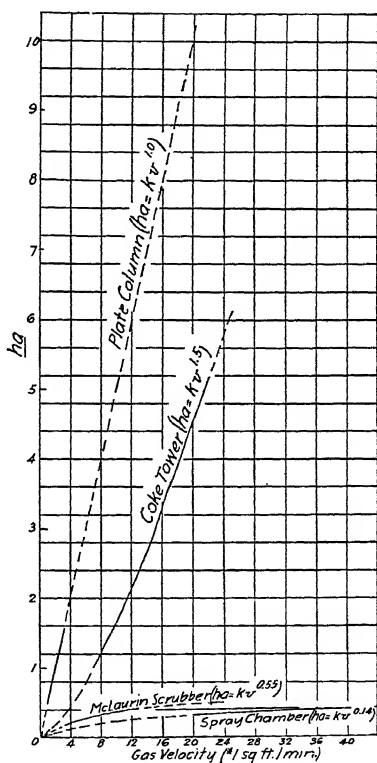
The water rate was expressed as pounds of water per square foot of cross-section of tower per minute.

The effect on the coefficients of absorption of changes in the rates of flow of gas and of liquid have

been studied, and the reader is referred to the previously mentioned article by Whitman and Keats³ for further information in this regard. In general, increasing velocities of gas cause nearly proportional increases in the absorption coefficient, while changes in the rate

FIGURE 95.

Coefficients of Heat Transfer for Scrubbing Towers.



of flow have less effect. It may be stated that, although there is little data yet available to prove it, the absorption coefficient becomes greater as the temperature rises because of decreased viscosity of the liquid, and that the molecular weight of the vapor being absorbed is also a factor.

The size of a scrubber required to conform to given

specifications may be determined from the foregoing equations. For other methods of computation, see Sherwood and also Walker, Lewis, McAdams and Gilliland.

Nomenclature

W = pounds of dry gas passing through the scrubber per minute.

w = pounds of scrubbing liquid used per minute.

H_0 = pounds of solvent entering the scrubber in the gas per pound of dry gas.

H_1 = pounds of solvent leaving in the gas per pound of dry gas.

P_0 = humidity of exit scrubbing liquor as explained below.

P_1 = humidity of entrance scrubbing liquor (usually zero).

t_0 = temperature of exit scrubbing liquor.

t_1 = temperature of entrance scrubbing liquor.

T_0 = temperature of entrance gas.

T_1 = temperature of the exit gas.

L = height of the scrubbing tower in feet.

A = total cross-section area of the tower in square feet.

ka = coefficient of diffusion of the vapor between the gas and the scrubbing liquid expressed as pounds per cubic foot of tower per pound humidity difference per hour.

ha = coefficient of heat transfer in B.t.u. per cubic foot of tower per degree F. temperature difference between the gas and the liquid per hour.

s = humid heat, as explained later.

The nomenclature used above is similar to that used by Grosvenor,⁴ in humidification and drying modified to suit the special conditions of scrubbing.

The humidity of the scrubbing liquid is expressed as pounds of solvent vapor per pound of gas when the partial pressure of the solvent vapor in the gas is the same as that above the liquid in question. This permits the partial pressure difference of the solvent vapor between the gas and the liquid to be expressed in pounds per pound of dry (solvent-free) gas, which is very advantageous in the following calculations.

The humid heat is the heat in B.t.u. needed to raise one pound of vapor-free gas, plus the solvent that it contains, one degree Fahrenheit.

⁴ *Trans. Am. Inst. Chem. Eng.*, 1908.

It should be understood that the coefficients ha and ka are over-all coefficients, combining the coefficients of diffusion and heat transfer of the gas films on the surface of the liquid and the diffusion of the vapor and the heat into the liquid after having passed through the surface film. In order to predict accurately the value of these coefficients for any particular conditions, the proper values of the film coefficients should be accurately known. This is not the case at the present time, although there is a great deal of research being conducted in this regard. It is therefore necessary, until these unobtained data are available, to make use of the approximate values already obtained and quoted above, and to make reasonable allowances to provide satisfactory factors of safety.⁵

In order to make the calculations of reasonable simplicity, the following assumptions are made. These assumptions are justifiable for most cases of solvent recovery by scrubbing, and in those cases where this is not true, allowance may be made after the completion of the calculations.

(1) Adiabatic operation, that is, where there is no heat taken from the tower during the operation, by cooling coils or by radiation and convection to the surroundings.

(2) The evaporation of the scrubbing liquid can be neglected.

(3) The increase in weight of the scrubbing liquid due to the solvent vapor that it picks up can be neglected.

Heat Balance

$$(57) \quad wdt = WsdT + Wr'dH$$

where r' (a negative quantity) is the heat of solution of the solvent vapor in the scrubbing liquid. This

⁵ For further information, see the following references: Walker, Lewis, McAdams and Gilliland, "Principles of Chemical Engineering," 1937; W. K. Lewis, *J. Ind. Eng. Chem.*, 8, 827 (1916); C. S. Robinson, *Trans. Am. Soc. Mech. Eng.* (1922).

equation may be integrated approximately by assuming that s and r' have average values between the limits between which the tower is working, giving

$$(58) \quad w(t_1 - t_0) = Ws(T_1 - T_0) + Wr'(H_1 - H_0)$$

Flow of Heat

$$(59) \quad WsdT = ha V(\Delta t) = ha AdL(T - t)$$

This equation may be easily integrated on the assumption that $(T - t)$ average is the arithmetic mean between the bottom and the top of the scrubber, which is very nearly true for counter-current operation, by which nearly all scrubbers operate, giving

$$(60) \quad Ws(T_1 - T_0) = ha A L \left(\frac{T_1 - t_1 + T_0 - t_0}{2} \right)$$

Diffusion of Solvent Vapor

$$(61) \quad WdH = ka A dL(H - P)$$

which may be integrated by assumptions similar to those made in (60), giving

$$(62) \quad W(H_1 - H_0) = ka A L \left(\frac{H_1 - P_1 + H_0 - P_0}{2} \right)$$

W. K. Lewis⁵ has shown that for towers of this type it is approximately true that

$$(63) \quad \frac{ha}{ka} = s, \text{ (closely enough for most engineering work)}$$

Therefore, by dividing (62) by (60) and substituting (63), there is obtained:

$$(64) \quad \frac{H_1 - H_0}{T_1 - T_0} = \frac{(H_1 - P_1 + H_0 - P_0)}{(T_1 - t_1 + T_0 - t_0)}$$

The application of these equations to counter-current scrubbing is made in the following manner.

In scrubbing operations the following known, established conditions are usually to be met:

- (a) The volume of gas per minute = W (expressed in pounds)
- (b) The weight of vapor in the gas = H_0
- (c) The fraction of the vapor to be recovered = $\frac{H_0 - H_1}{H_0}$
- (d) The temperature of the scrubbing liquid entering = t_1
- (e) The solvent humidity of the scrubbing liquid entering = P_1 (usually zero)
- (f) The temperature of the gas entering = T_0
- (g) ka and ha must have been previously determined by experiment on a tower similar in construction to that which it is proposed to use.

The unknown relations are therefore:

- (h) The weight of the scrubbing liquid = w
- (i) The temperature of the exit liquid = t_0
- (j) The solvent humidity of the exit liquid = P_0
- (k) The temperature of the exit gas = T_1
- (l) The volume of the scrubber = $Al = V$

The solvent humidity of the exit liquid, P_0 , depends upon the weight of the solvent vapor dissolved in the liquid during its passage through the tower, the weight of the scrubbing liquid, and the temperature, t_0 . This may be expressed by the following equation:

$$P_0 = \text{function of } t_0, (H_0 - H_1), \text{ and } \frac{W}{w}$$

Since the relation between the pressure and the temperature is complicated (Clapeyron equation), it is difficult, though possible, to work with the temperature t_0 unknown, and it is better to take t_0 as known and to determine the necessary value of t_1 to make the conditions fit the other known values stated above. This has the added advantage that P_1 is usually zero, thus disposing of another unknown quantity.

Size of Scrubber

The size of the scrubber may be determined directly from equation (62) in terms of one other unknown, w . This may best be shown by means of an illustration, scrubbing acetone from air by means of water. Therefore take the following quantities as given:

W , weight of air per minute = 100 lbs.

H_0 , humidity (acetone) of the entering air = 0.069 lb. of acetone per pound of acetone-free air.

H_1 , humidity of exit air (90% recovery) = 0.0069 lb.

T_0 , temperature of entering air = 80° F.

t_0 , temperature of exit water = 80° F.

ka , for an air velocity of 500 ft. per min. in slat-filled towers = - 0.4.

P_1 , humidity of entering water (assume acetone-free water) = 0.

To calculate P_0 , proceed as follows:

Molecular weight of acetone = 58.

Vapor pressure of pure acetone at 80° F. = 260 mm.

The vapor pressure of acetone over dilute solutions may be figured from Henry's Law, using data from *Z. Physik. Chem.* 39, 485 (1902). The effective partial pressure of acetone being 2.0 times its true vapor pressure multiplied by its mol fraction = $2 \times 260 \times x$.

Henry's Law gives the equation:

$$p = 2 \times 260 \times \frac{\frac{W(H_0 - H)}{58}}{\frac{w}{18}} \quad (\text{the partial pressure});$$

substituting the proper value of W and $(H_0 - H_1)$, there is obtained the relation:

$$p = \frac{1000}{w}.$$

therefore, assuming normal barometric pressure, 760 mm.,

$$P_0 = \frac{58p}{29 \times (760 - p)} = \frac{2000}{760w - 1000}$$

where 29 is the molecular weight of air.

Equation (62) would therefore give

$$100(0.069 - 0.0069) = .04AL \frac{2000}{760w - 1000} \quad 0.0069 - 0. + 0.069 - 1760w - 1000$$

$$\text{whence} \quad AL = \frac{23,550w - 31,000}{57.7w - 2076}$$

This relation between AL and w can best be shown in the form of a curve as in Figure 96.

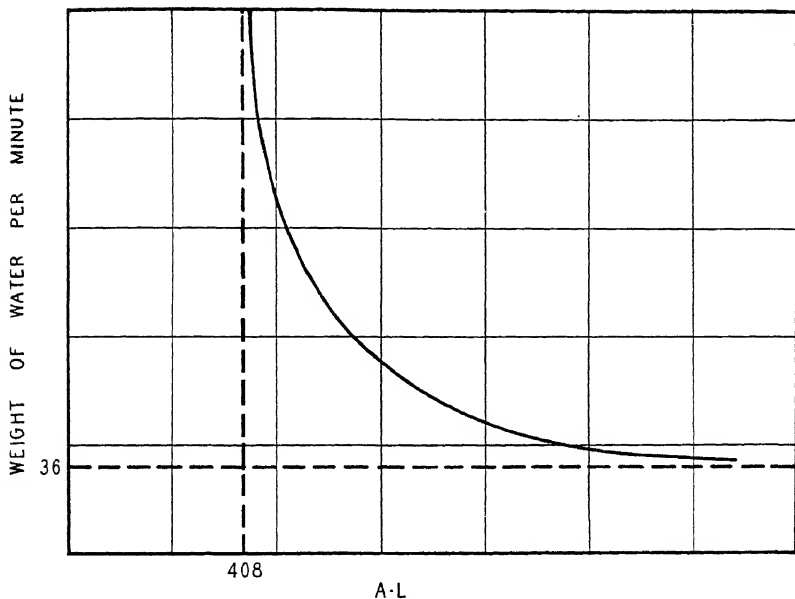


FIGURE 96.

This curve indicates that a scrubber operating under the chosen conditions can recover 90 per cent of the acetone only when its volume is greater than 408 cubic feet and when it is using over 36 pounds of water

per minute, the necessary amount of water required being read off the curve as shown.

The selection of the most economical size of tower should be the result of an economic balance between the cost of the tower per unit product and the cost of operating it as indicated in Figure 97, the total cost per unit being the sum of the two costs shown. The size of the tower corresponding to the lowest point on the curve is the most economical one to use. The basis for such an economical balance is the curve in the first figure.

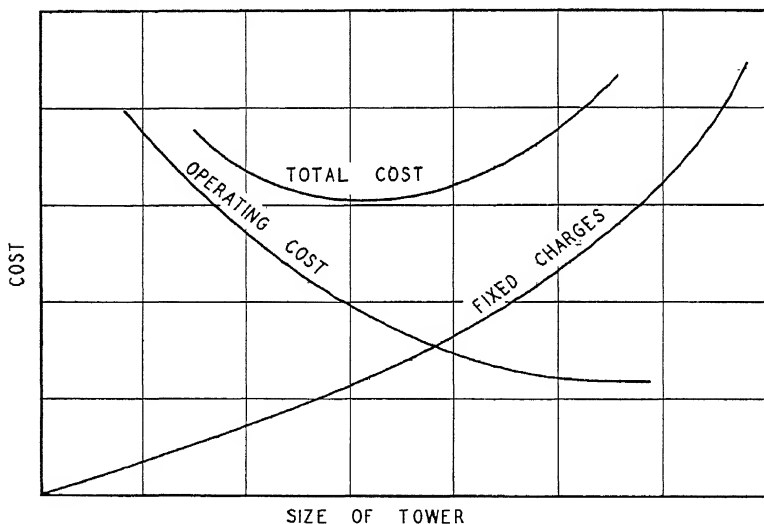


FIGURE 97.

Temperature of the Scrubber Water

The temperature of the liquid leaving the tower was selected to be 80° F. It is therefore necessary to calculate the temperature of the feed water which would be needed to produce this desired temperature. This may be done by solving simultaneously equations (60), (62), and (64), giving the relation:

$$(65) \quad W = \frac{\frac{w(t_1 - t_0)}{s(2T_0 - t_1 - t_0) + r'(2H_0 - P_1 - P_0)}}{1 + \frac{2w(t_1 - t_0)}{ka AL s(2T_0 - t_1 - t_0) + r'(2H_0 - P_1 - P_0)}}$$

Note: This equation seems complicated, but when the proper values for the letters are substituted, it becomes very simple.

If now proper values for w and Ax have been selected from an economic balance based on the curve shown above, the suitable values may be substituted in equation (65), and t_1 , the feed temperature required, determined.

Thus in the example given, the substitutes are as follows:

$r' = -310$ (heat evolved) B.t.u. per lb. (Landolt-Börnstein).
 $s = 0.25$, approximately.

Suppose that w and Ax have been chosen as 100 and 630 on the basis of the economic balance referred to, respectively, then

$$P_0 = \frac{2000}{760 \times 100 - 1000} = 0.0267 \text{ and}$$

$$100 = \frac{\frac{100(t_1 - 80)}{0.25(160 - t_1 - 80) - 310(0.138 - 0 - 0.0267)}}{1 + \frac{200(t_1 - 80)}{-0.4 \times 630 \times 0.25(160 - t_1 - 80) - 310(0.138 - 0 - 0.0267)}}$$

Solving for $t_1 = 63.1^\circ \text{F.}$, a temperature rise of 17° .

In a similar manner, the temperature of the air leaving the scrubber may be calculated.

The author has recalculated the values given by Whitman and Keats for ka and has added some values obtained by himself, and believes that the following values are as close an approximation to the fact as it is possible to obtain from the very incomplete data available at present.

In this table, ka is given for water at ordinary room temperature and for air velocity of one pound per square foot of cross-section of tower per minute. In

the absence of better information, it may be assumed that the value of ka is proportional to the gas velocity and inversely proportional to the relative viscosity of water at 68° F. Thus in a coke-filled scrubber operating at an air velocity of 0.1 pound of air per square foot of cross-section of tower per minute, and using a wash oil whose relative viscosity was 50, the value of ka to use in the foregoing equation would be:

$$\frac{10.0 \times 0.1}{50} = 0.02$$

A much better way to determine the value would of course be to run a small-scale scrubbing experiment, if possible on the same type of scrubber, using the oil which would be used in the actual plant, and substantially the same gas velocity, thereby determining the value of ka and substituting that in the equation.

The pressure drop to be expected is expressed in inches of water per foot of height of tower when the gas velocity is 0.1 pound of gas per square foot per minute. The actual pressure drop can then be calculated from the formula:

(66)	pressure drop — $\frac{WL}{\Delta p}$	ka	Δp^*
Plate scrubber with boiling caps		5.0	1.0
Centrifugal scrubber		2.1	.0016
Slat-filled scrubber		0.2
Spray scrubber		0.3	.0015
Coke-filled scrubber (3" lumps)		10.0	.0057

*These pressure drops are for water rates of ordinary magnitude; changes of any magnitude in the rate will affect the pressure drop considerably.

The pressure drop in plate towers is practically constant over moderate changes in gas velocity, on account of the fact that the static head of the liquid comprises the bulk of the resistance to flow of gas.

The foregoing calculations were based on the assumption that the operation of the tower was adiabatic, that is, that there was no external cooling of the gas or liquid while it was in the tower. The calculation

indicated that a temperature rise of approximately 17° F. could be expected. A rise of this amount would not be serious in most scrubbing operations, but if the gas had been richer in acetone, so that a richer solution could have been obtained from the bottom of the scrubber, the temperature rise would have been considerably greater, invalidating to a considerable extent the calculations, and also interfering with the effectiveness of the scrubber on account of the rise in the temperature of the water and the corresponding increase in the vapor pressure of the dissolved solvent.

Under such circumstances it is almost always necessary to cool the gas or the liquid or both during their passage through the scrubber. This has been done in two ways. Cooling coils are frequently installed in the tower. The other method consists in withdrawing the liquid a number of times as it travels down through the tower and cooling it by means of outside cooling coils. The former method is the better for small installations, and the latter is the better for large units. The methods to be used in the calculation of the cooling surfaces for such coolers are identical with those described under the design of condensers, and the reader is referred to that section.

If the cooling in the tower is sufficient to keep the scrubbing liquid at substantially constant temperature, the size of the tower may be figured as before from equation (62), while the calculation of the temperature rise is of course unnecessary.

Usually cooled towers will lie immediately between the two extremes of complete cooling and adiabatic operation.

Chapter 24

Scrubbing Apparatus

Scrubbing Towers

The function of the scrubbing tower in a solvent recovery plant is to bring the gas carrying the solvent vapor into intimate contact with the scrubbing liquid. This contact may be either counter-current or parallel current, usually the former. It is usually continuous, although certain systems employing intermittent operation with respect to the scrubbing liquid have been put into more or less successful operation.

The continuous counter-current scrubber is usually of the vertical type, making use of the fall of the scrubbing liquid due to gravity, with the gas rising under pressure from a fan or blower.

The simplest form of this type of scrubber is the filled type, a vertical, usually cylindrical shell containing various forms of filling or packing. The filling may be lumps of stone or coke, or it may consist of special manufactured forms, either dumped in, as is the case with the small hollow cylinders known as Raschig rings, or carefully packed, as is the case with the special forms made for the acid and allied industries.

The coke tower has a high coefficient of absorption and is very satisfactory for nearly all materials. It has, however, one disadvantage. Unless very great care is taken the coke will pack unevenly in the tower. This means that the flow of liquid and gas will not be uniform over the entire cross-section of the tower and that the contact between them will be poor. This by-passing can be avoided to a considerable extent by carefully screening the coke to one size before dumping it into the tower. For large towers the lumps should be from

three to four inches in size, whereas for smaller towers, smaller sizes down to $\frac{1}{4}$ -inch diameter are suitable. The second cause of uneven distribution is the method of applying the scrubbing liquid on top of the coke. Formerly a bank of perforated pipes or troughs was popular, but these have been superseded to a considerable degree by pressure sprays, delivering solid cones of spray and so arranged to apply the liquid uniformly over the entire top surface of the coke. The coke should not extend to the bottom of the tower, but should be supported on a metal or wooden grid above the bottom, preferably high enough to enable a man to crawl in to inspect the grid, a suitable man-hole being provided for this purpose. The towers are usually constructed of steel, but the author believes that in most cases wooden towers would be just as satisfactory and considerably less expensive to install and maintain.

The use of Raschig rings made of suitable materials, metals, glass, carbon, or stoneware (small hollow cylinders whose length equals the diameter) has permitted the operation of towers having the low pressure drop of the coke tower with considerably improved distribution on account of the uniformity of the filling. These rings should be carefully dumped into the towers when the latter are full of water, thus diminishing breakage.

Special stoneware fillings carefully placed by hand are less frequently used in solvent recovery work on account of their expense. They insure, however, very uniform gas and liquid distribution with low pressure drop.

For large installations where a very low pressure drop must be had, the slat tower is very popular. In such a tower the surface exposed to contact is practically the surface of the slats, and this type of tower requires very uniform distribution of the scrubbing liquid at the top to insure satisfactory operation.

A number of horizontal scrubbers are on the market, such as the horizontal ammonia washers used in

gas works. The chief advantage of these is the low pressure drop available, but their absorption coefficients are probably low.

Plate scrubbers are very efficient in bringing the liquid and the vapor into contact. They operate, however, under considerable pressure drop, due to the static head of liquid on the plates, which must be overcome. These towers are of the perforated plate or of the boiling cap plate type.

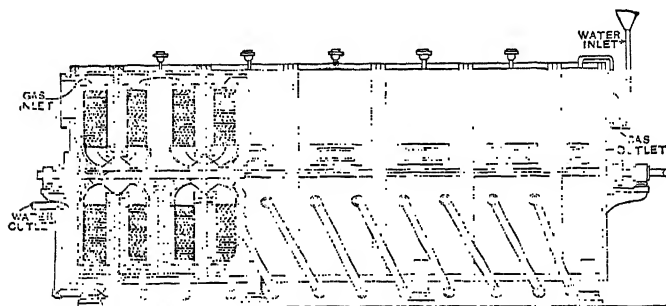


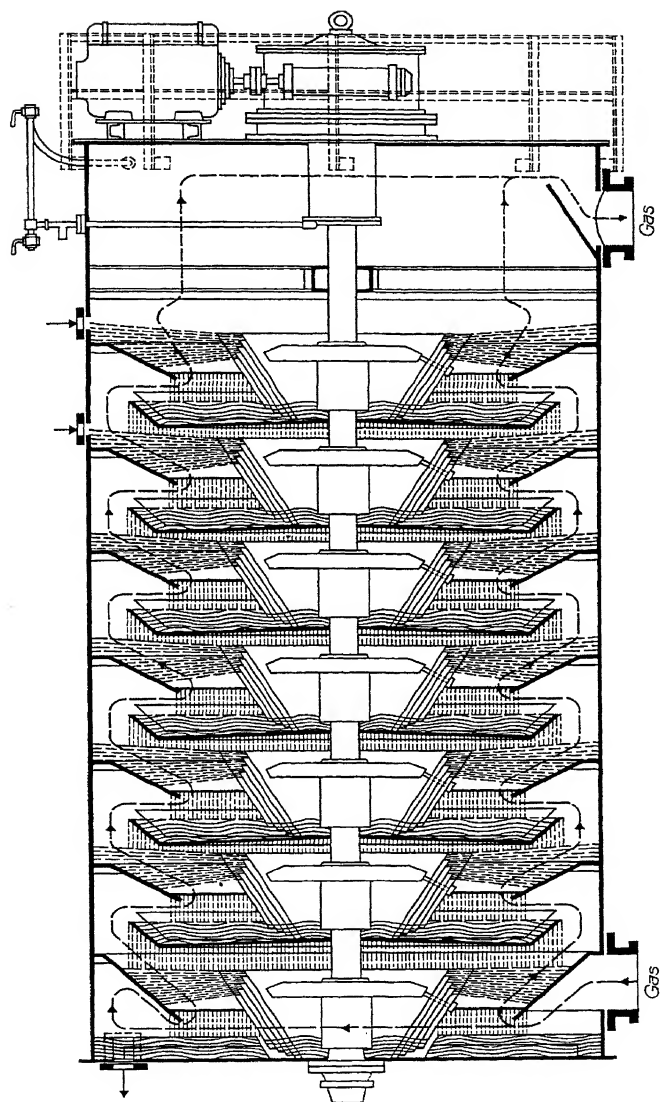
FIGURE 98. Horizontal Gas Scrubber (from Rogers "Industrial Chemistry").

The former are efficient if operated within their working range, but if the gas velocity falls too low, the plates will drain through the holes, and the scrubbing action will nearly cease. The plates must also be very carefully leveled. For large sizes they are less satisfactory than the boiling cap type, which are however, considerably more expensive.

The latter are much more flexible in operation, it being possible to vary the gas and liquid rates over wide ranges without seriously interfering with the operation.

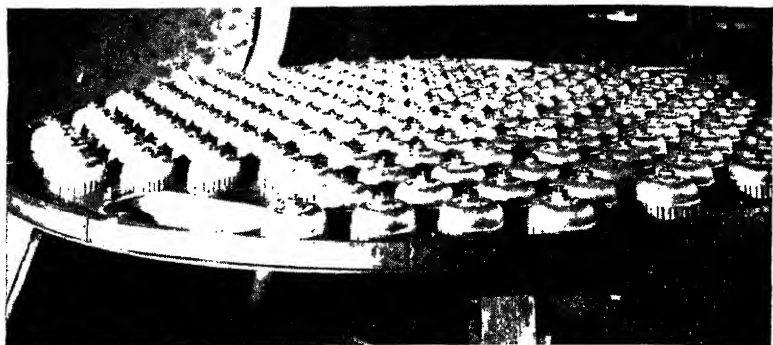
The customary velocities used in the various types of scrubbing towers are given in the following table:

Plate towers	1 ft. per sec.
Slat towers	10 ft. per sec.
Coke towers	2 ft. per sec.



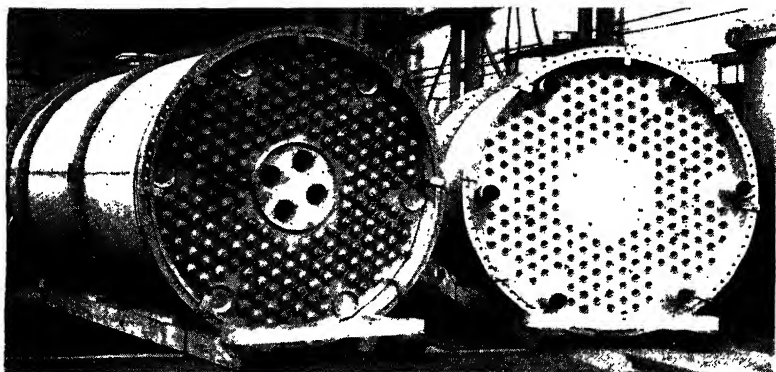
Courtesy Koppers Co.

FIGURE 99. Scrubbing Tower.



Courtesy Vulcan Copper & Supply Co.

FIGURE 100. Plate from Boiling Cap Type of Scrubbing Column.



Courtesy Vulcan Copper & Supply Co.

FIGURE 101. Boiling Cap Type Scrubbing Column, end view.

These velocities can be increased or decreased at the expense or gain of back-pressure, as indicated in the previous chapter.

The rate of flow of liquid is limited only by that amount that will flood the tower, this amount depending on the design and the rate of flow of air. The water rates indicated in the previous chapter are about the usual ones in practice.



FIGURE 102. Close-up of Individual Boiling Cap.

Variation in Concentration

In many industries, especially those where unit operations are semi-intermittent, the concentration of the solvent in the air leaving the plant is subject to considerable variation. This is illustrated in Figure 103 constructed from data obtained in a French plant making smokeless powder.

The average height of the curve was found by means of a planimeter to be 31.0 grams per cubic meter. The apparatus would therefore be designed on that average concentration as a basis.

In actual operation, the loss of solvent due to non-absorption will be greatest at the peaks of the curve, but if scrubbing conditions remain constant, the percentage loss should remain nearly constant at all times. Constant scrubbing conditions would be obtained in cases similar to the one given, where the variations in concentration were over short time intervals. But in

those cases where the variation occurs relatively infrequently and the concentration remains substantially constant over considerable periods of time, it is customary to modify scrubbing conditions to suit the concentration. This may be done most easily by changing the rate of feed of scrubber liquor so as to produce a

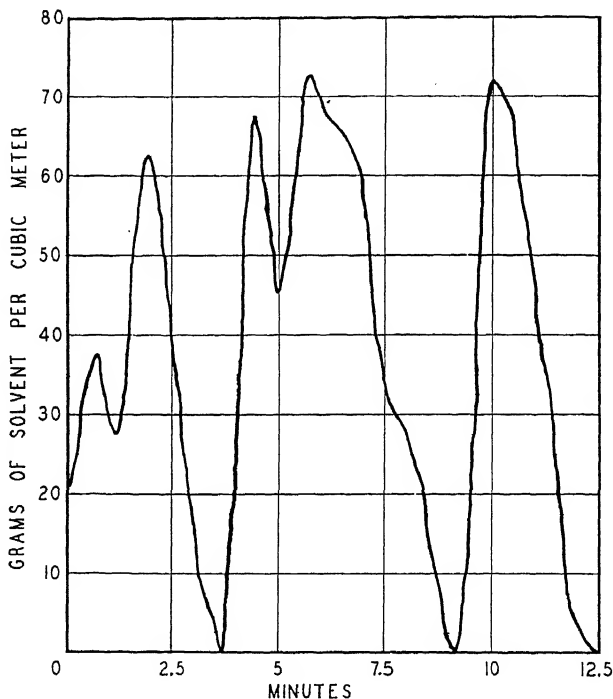
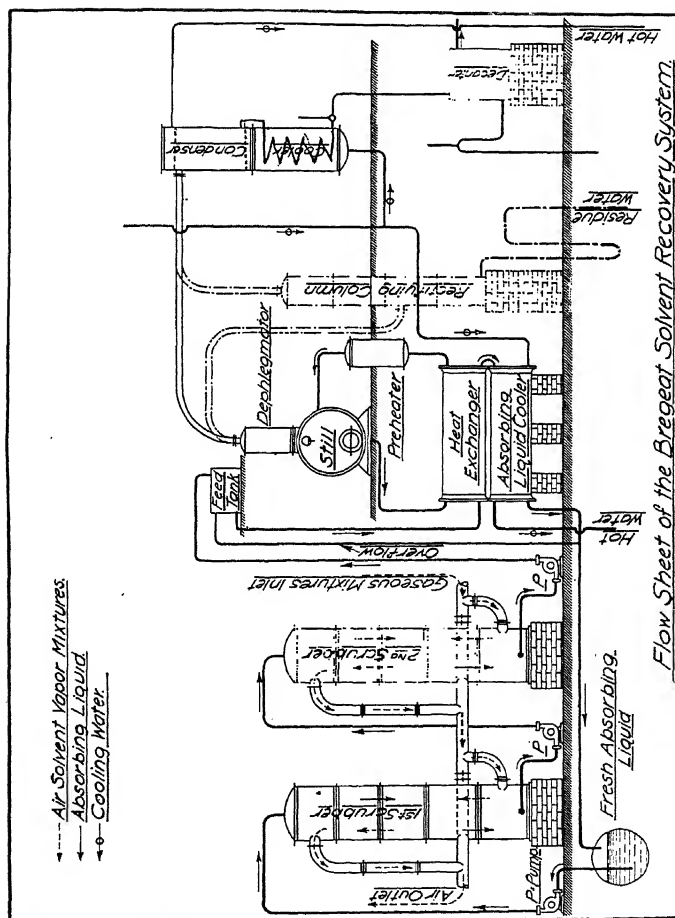


FIGURE 103.

more uniform concentration of solvent in the scrubber liquor leaving the absorption apparatus. The difficulty of this method lies in the necessity for continual attention on the part of the operator, although it is quite possible to design automatic feed controls to take care of the change in concentration of the effluent liquor.

FIGURE 104.
Example of
Scrubbing System
for Solvent Recov-
ery.



Illustrations of Plants

An example of a simple installation for scrubbing is given by the Bregeat absorption system illustrated in Figure 104.

The scrubber in this case is in two sections to save head room, making it necessary to pump the scrubbing liquid from the bottom of one section to the top of the other. This permits the use of either section alone if necessary. The scrubber is connected with a continuous still as was shown in Figure 94, the design of which is varied to suit the character of the solvent. The solid lines indicate the arrangement when the solvent is insoluble in water, while the dotted lines are for a soluble substance such as alcohol.

Chapter 25

Special Absorbents

The use of liquids as absorbing media for solvent vapors has been discussed in previous chapters. There is a special case of absorption which should be discussed separately, namely, where the absorbing liquid and solvent react chemically with the formation of a less volatile compound.

The most common example of such an absorbent is sulphuric acid, which is used for absorbing the combined vapors of alcohol and ether from air. These two substances combine with the sulphuric acid to form a less volatile substance called ethyl sulphuric acid, which can be decomposed afterwards, regenerating the sulphuric acid and liberating a mixture of ether and alcohol, the relative proportions of which in the resulting vapor depend upon the concentration and temperature of the ethyl sulphuric acid. As the process is usually carried out, a considerable proportion of the alcohol absorbed by the acid is liberated in the form of ether. It so happens in such cases, on account of the great volatility of the ether, that the percentage of that gas in the original gas actually absorbed by the acid is considerably less than that of the alcohol absorbed, so that the portion of the alcohol recovered which is in the form of ether does not wholly make up for the ether loss in the original process, and therefore there is no accumulation of ether by the system at the expense of alcohol. Actually, there is a considerable net loss of both alcohol and ether which has to be made up from some outside supply.

The use of sulphuric acid for absorbing these two solvents was very common in Europe, but is not used

in the United States. Although it has many advantages, notable among which is the very low vapor pressure of these solvents over their solution in it, the very great difficulty of handling such a corrosive liquid, and the necessity of reconcentrating it after each time it is used, make its use exceedingly troublesome and expensive. The author has been informed that it has been superseded by other processes, notably solid adsorption on activated carbon.

Its theoretical interest is such, however, that the author has included a series of curves, which have been very kindly placed in his hands by the Bregeat Corporation, showing the effects of temperature and dilution on the solubility of these solvents in sulphuric acid.

Figure 105 is based on data furnished by the Bregeat Corporation. It represents the solubility of ethyl ether in several solvents at 20° C., except butyl alcohol, which is at 15° C. This diagram is given for the purpose of showing the effect on the solubility of a substance in a solvent of the chemical relations between them.

It is known that if two volatile liquids have a tendency toward immiscibility, the partial pressure of each above a mixture of the two is greater than that calculated from Raoult's Law, whereas if there is a tendency toward chemical combination, the partial pressures will be less than that calculated from Raoult's Law. Frequently both effects are combined, giving great irregularities.

This is illustrated in the present case. The concentration of ether in sulphuric acid which would give a partial pressure in the vapor in equilibrium with it at 20° C. of 50 mm. is about 10 per cent by weight according to Raoult's Law, while the actual concentration is something above 60 per cent, because of the tendency for the combination of the ether and acid to form ethyl sulphuric acid.

In a similar manner *m*-cresol (the chief constituent of the Bregat absorbent) will absorb ether at 20° to a concentration of 35 per cent, whereas according to Raoult's Law, a partial pressure of 50 mm. corresponds to 8.5 per cent.

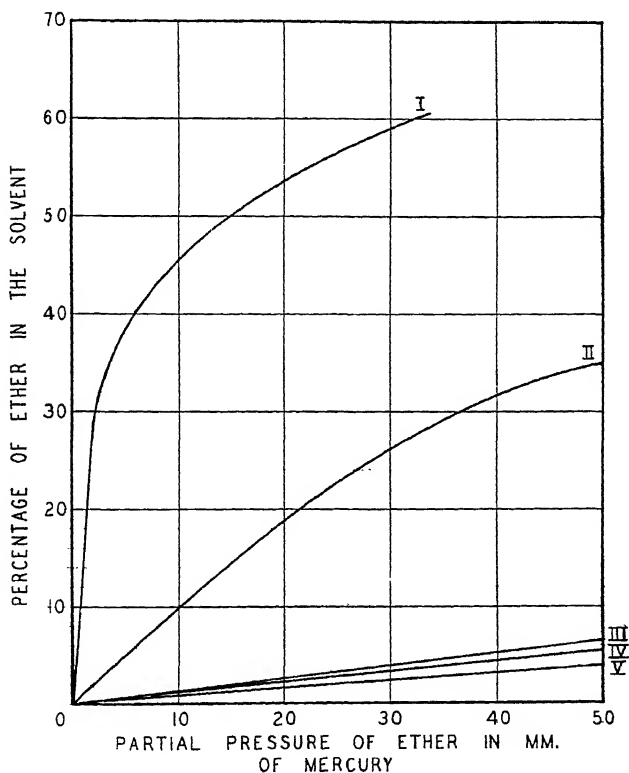


FIGURE 105.

On the other hand, the concentration corresponding to 50 mm. for ether in ethyl alcohol should be 18.5 per cent by Raoult's Law, whereas it is actually about 4 per cent, indicating a distinct tendency toward immiscibility. This tendency is less marked in the case of amyl

alcohol, but is actually existent in the case of water, which is often considered the lowest member of the alcohol series. Mixtures of ether and methyl alcohol should show even greater deviation than is the case with ethyl alcohol.

It should be the object of designers of absorbing equipment, therefore, to select as absorbing liquids those which have the tendency toward chemical combination, rather than the reverse, since the amount of absorbing liquid required for a given problem and the size of the absorbing equipment will be considerably lessened thereby. But care should be taken that the subsequent recovery of the solvent by distillation is not too difficult.

Another factor of importance in the selection of the absorbing liquid is the inevitable presence of water vapor in the gas carrying the solvent vapor. The ideal absorbing liquid should be unaffected by the presence of water. Such a liquid would therefore be one in which water is substantially insoluble, as is the case with the members of the benzene and the methane series of hydrocarbons. Those liquids which absorb water readily will frequently do so at the expense of the solvent. This effect in the absorbing of ether by sulphuric acid is shown clearly in the accompanying diagram, Figure 106, which is similar to the preceding one, for acid of several strengths, indicating that 60-per cent acid has but one-third of the absorbing power for ether of that of 100-per cent strength.

The selection of the best absorbent for a particular case should be the result of an economic balance involving the cost of the recovery of the solvent plus the value of the lost solvent and the losses of absorbent, and the cost of the equipment required. The author has repeatedly emphasized the fact that every solvent recovery problem has features different from any other problem, and it is very unusual that the apparatus designed for one special case will be the best for any

other case. This is just as true in the case of the selection of the absorbent liquid, and therefore the greatest care should be used in making the selection. Unless actual experience with very similar cases is available,

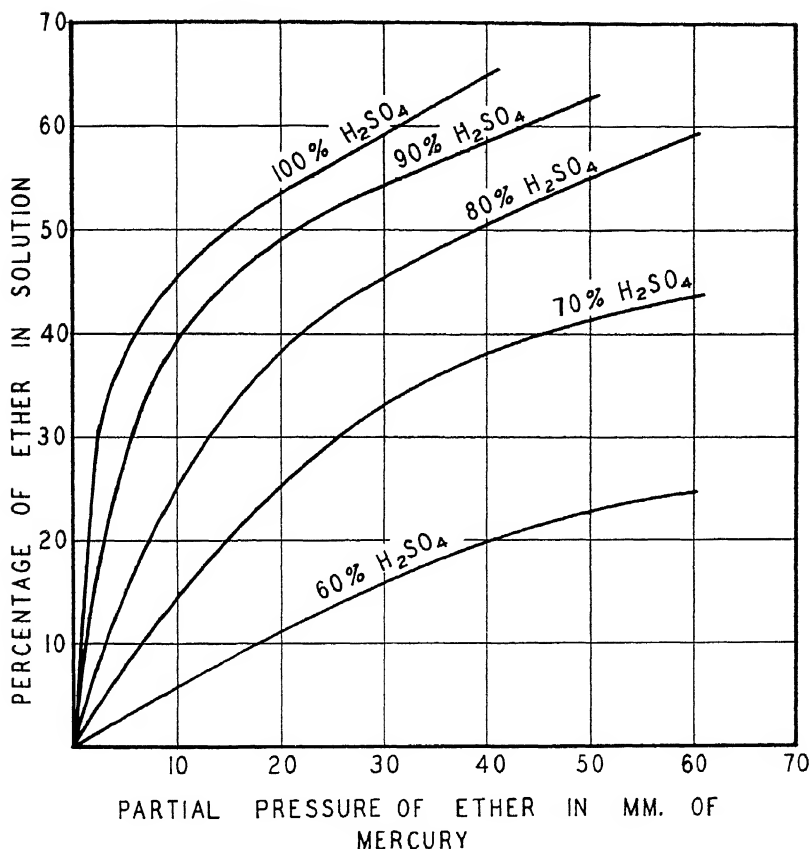


FIGURE 106.

the author strongly advises the installation of an experimental laboratory scrubber in which suitable liquids and solids may be tested. Such experiments form the only sure basis for satisfactory design.

Acetone Recovery by Sulphuric Acid

W. R. Ormandy * has described a process for the recovery of acetone from air by means of sulphuric acid. The following table gives the equilibrium relationship between various strengths of acid at 15° C. and air containing several concentrations of acetone.

cc. of acetone per 100 cc. of H ₂ SO ₄	Specific Gravity of Sulphuric Acid					g. of acetone per cu. meter of air
	1.55	1.575	1.60	1.625	1.65	
1	0.6	0.4	0.31	0.23	0.13	
10	7.7	5.6	4.1	2.81	1.80	
20	16.5	12.7	9.7	6.7	4.6	
30	26.5				8.5	
40	40.5				14.2	

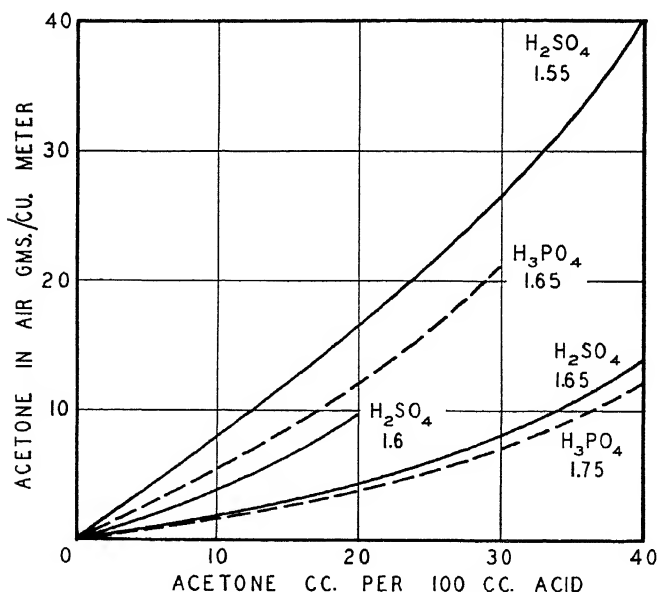


FIGURE 107.

These figures as well as corresponding figures for phosphoric acid are plotted in Figure 107.

* *Trans. Ind. Chem. Eng.*, p. 80 (1929).

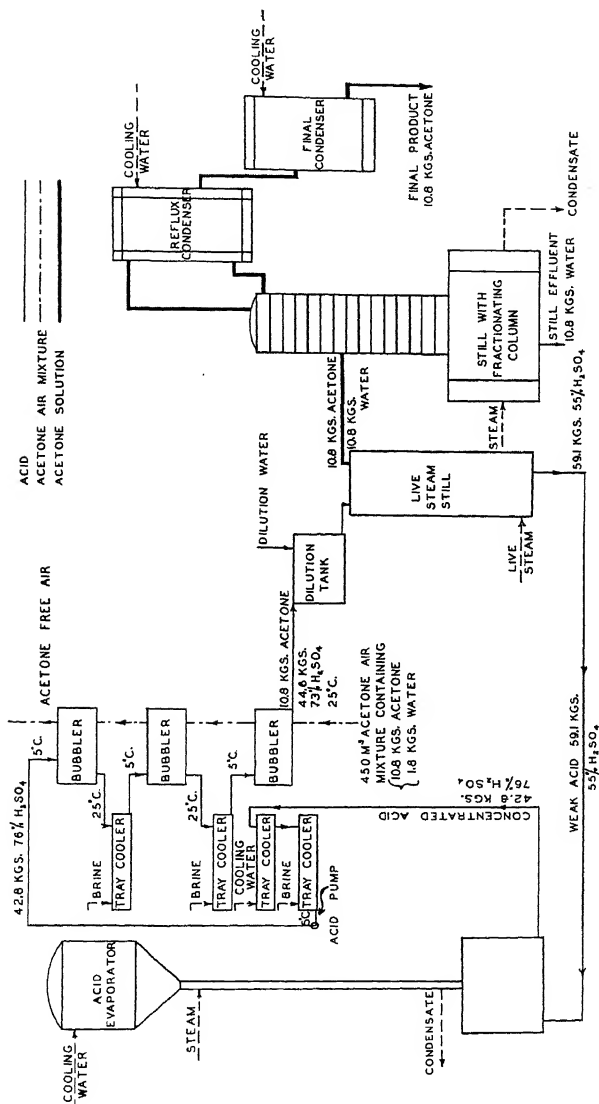


FIGURE 108.

The plant layout in Figure 108 is based on laboratory experiments and the amounts of material at each point in the process were calculated by proportion. It is necessary to keep the sulphuric acid containing the acetone below a temperature of 25°C . to prevent decomposition of the acetone. This is done by withdrawing the acid from the absorbing column when it reaches that temperature and running it through a brine cooler to reduce its temperature to 5°C . The acetone-rich acid from the bottom of the scrubbing tower is diluted with water and then fed to a stripping still where the acetone is stripped from it by open steam. The dilute, acetone-free acid then goes to a concentrator to be concentrated for reuse, while the mixture of acetone and water vapors from the top of the stripping still goes to a concentrating still where the two are separated. The calculations are based on 100 per cent recovery of the acetone.

The Bregeat Process

As noted previously, the Bregeat process makes use of cresol as its special absorbing agent for solvents soluble in water, but prefers the use of tetrahydronaphthalene, or "Tetralin," for solvents insoluble in water, although cresol will serve fairly well. The latter substance has about three times the absorbing capacity of ordinary petroleum wash oil for benzol vapors and therefore would require a smaller plant for the same percentage recovery, or recover more for the same size plant. Figure 109 shows a Bregeat plant used for recovering gasoline from casing-head gas, the tall tower being the absorbing tower and the taller building housing the fractionating equipment. Figure 110 shows another Bregeat plant for the removal of light oil from coke-oven gas. The Bregeat absorbing towers are filled with a special spiral packing which is shown in Figure 111.

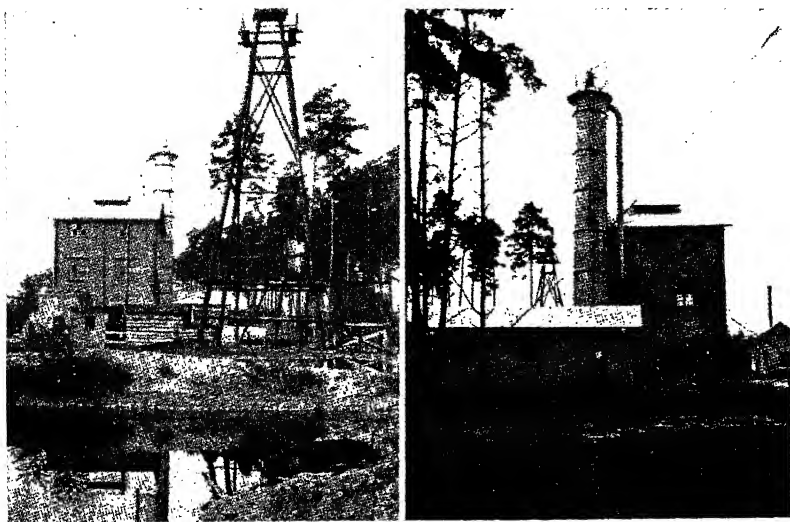


FIGURE 109. Extraction of gasoline from casing head gases by means of Tetralin.

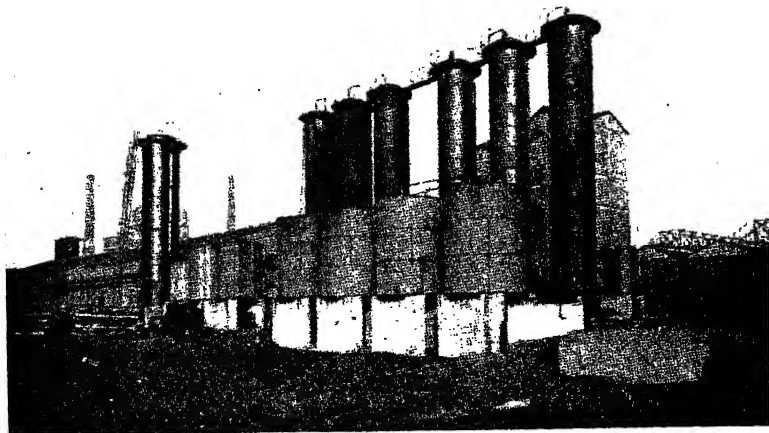


FIGURE 110. Washing Towers for the Removal of Benzol from Gas at the Seine (France) Coke Plant (Egrot & Grangé Method).

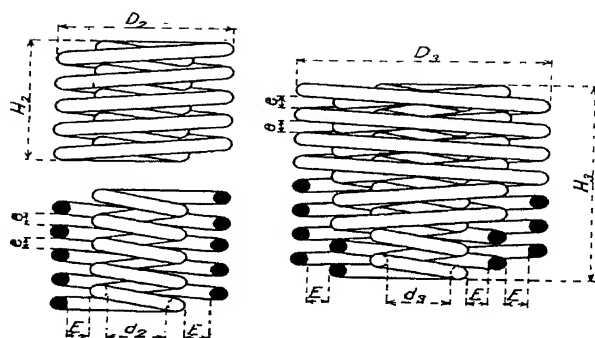


FIGURE 111. Bregeat Coils.

Chapter 26

Extraction by Solvents

The extraction of oils and fats by means of volatile solvents involves the recovery of the solvent in two ways, first, its separation from the extracted oil, usually by means of distillation, which is not in the province of this book, and the second, its separation from the residual extracted solids. The latter may be accomplished in three ways.

The first method is that of the displacement of the liquid solvent adhering to the solid by means of another liquid such as water, in which the solvent may or may not be soluble. This method has been successfully applied in several industrial installations, one excellent example of the method being that of the displacement of the ether from smokeless powder grains by means of liquid alcohol. The essential features for the successful operation of this method consist in using slow upward displacement with a liquid whose specific gravity is greater than that of the displaced solvent, taking every precaution to avoid mixing, either by convection currents or by stirring. Furthermore, since stirring must be avoided, it follows that the method will work only with solids which have uniformly distributed openings between the particles, other solids giving unequally distributed flow and by-passing, with the corresponding imperfect removal of the solvent. It should also be noted that in any case that portion of the displaced solvent last leaving the container will consist of a mixture of the two liquids and will require separation, by decantation if the liquids are immiscible, or by fractional distillation if they are miscible.

The second method of recovering the solvent from

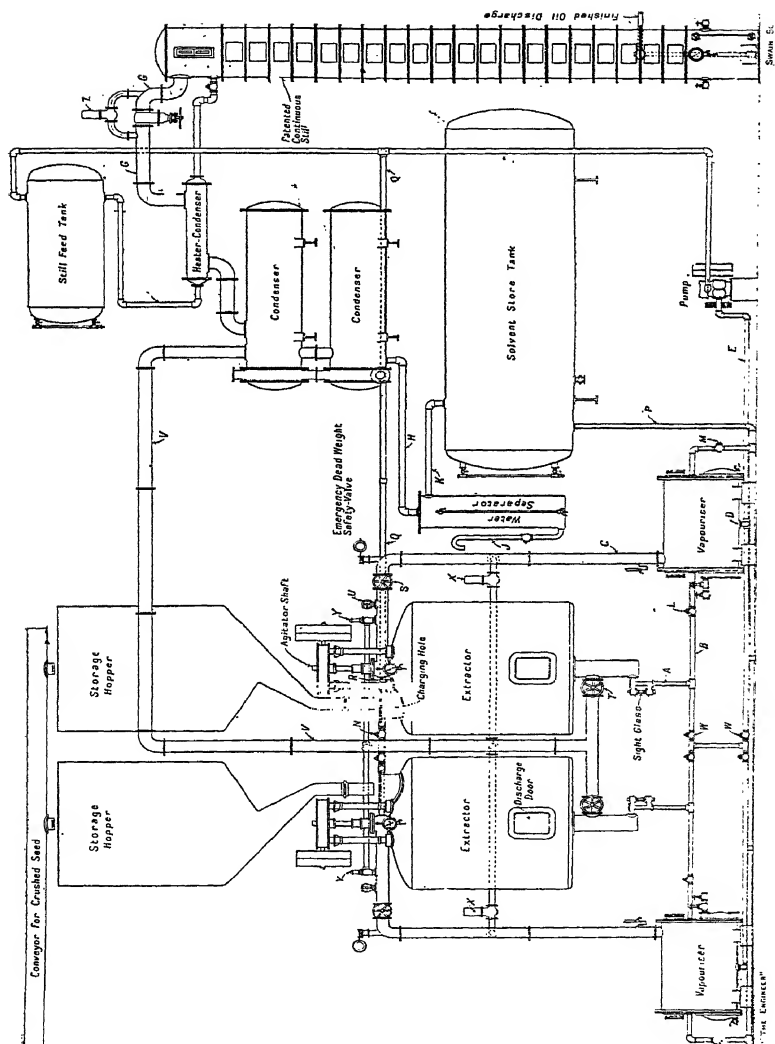
the extracted solid makes use of the direct application of heat by contact with hot walls, pipes, or direct radiation. The mechanism of this process has been discussed in some detail in Chapter 17. The essential thing with respect to this method is the continual movement of the solid past the source of heat. This is necessary on account of the extreme slowness with which heat flows through dried solids. There are in general two methods by which this can be accomplished, the first consisting of the use of a plow or scraper which continually brings fresh solid into contact with the heating surface; the second makes use of a rotary drum or kiln into which the moist solid is introduced, either continuously or intermittently, the walls of which are heated externally. The author has seen both methods in successful operation.

The third method, recovering the solvent from the extracted solids, is the one most commonly used, either alone or in combination with the second method; it involves circulation through the moist solid of a gas or vapor to furnish part or all of the heat of vaporization, to assist in bringing the heat more readily into contact with the solvent, and to decrease the partial pressure required for the solvent to vaporize. The effect upon the temperature required for vaporization has been discussed in Chapter 17. It remains, therefore, to state that it makes no difference in the vaporization whether a gas or a condensable vapor is used, this affecting only the problem of subsequent condensation. On account of the relative ease of handling a condensable vapor, such vapors are almost always used, the most common one being steam, either saturated or superheated, depending on the temperature required.

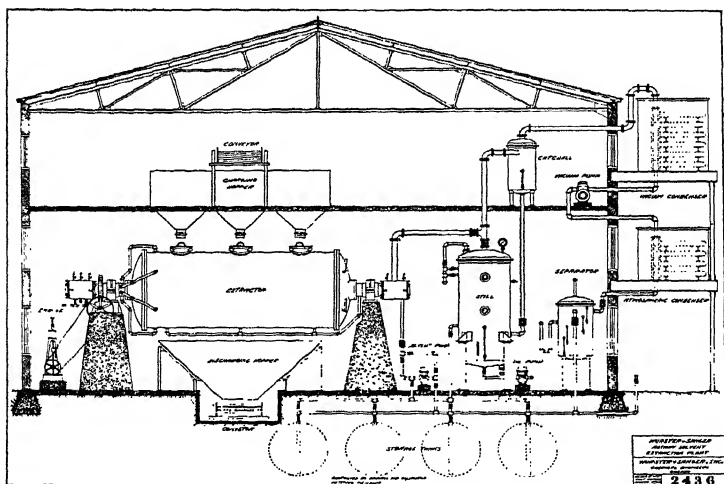
Steam under considerable pressure may in many cases be counted upon to furnish enough mixing and stirring of the solid, when released with its correspondingly considerable velocity, to obviate the necessity for mechanical mixing otherwise required. It is frequently

EXTRACTION BY SOLVENTS

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Scott
action



true, however, that mechanical plows, scrapers, or stirrers are desirable for the purpose of cutting down the time of contact necessary and the consequent steam consumption. Which method is best is wholly a question of the special problem and of the design of the extractor, bottom-dumping extractors usually making use of the scraper type, and side-dumping extractors using the plow, which gives automatic discharge of the dried solid when the outlet gate is opened. Basket-type extractors are, so far as the author knows, used without



Courtesy Wurster and Sanger, Inc.

FIGURE 113. Rotary Solvent Extraction Plant.

mixers of any kind; they depend upon the percolation of the steam into the interior of the mass.

An excellent example of a complete oil extraction plant (Ernest Scott and Sons) is shown in Figure 112.

In this apparatus the residual solvent is removed by blowing steam through the extractor. The steam is blown downward at the start to assist in the removal of the heavy vapor by downward displacement, and after the bulk of the solvent has gone to the condensers

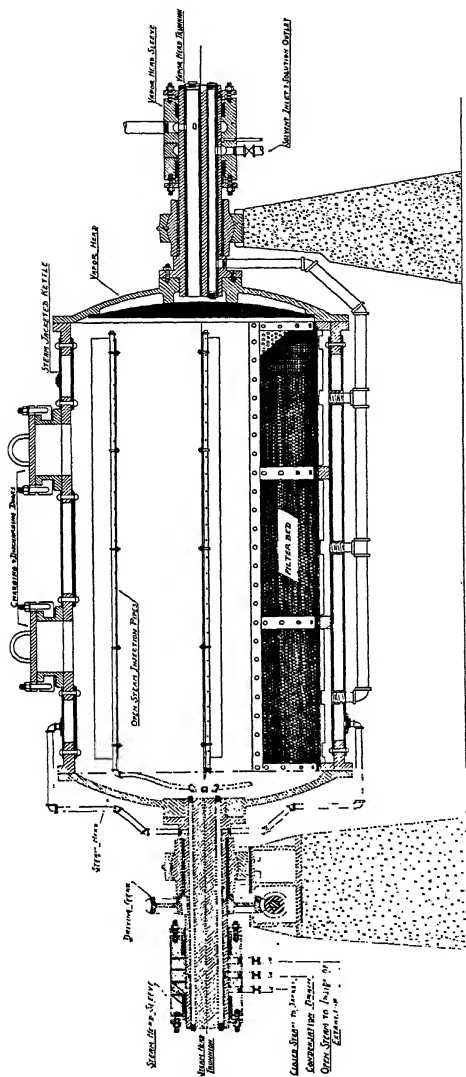


FIGURE 114. Cross-section of Rotary Extractor.

Courtesy Wurster and Sanger, Inc.

the direction of the steam is reversed, the mixed vapors passing out of the top of the extractors to the condensers as before. The condensed benzol vapors, together with the water, are separated by decantation as described in a previous chapter. A complete descrip-

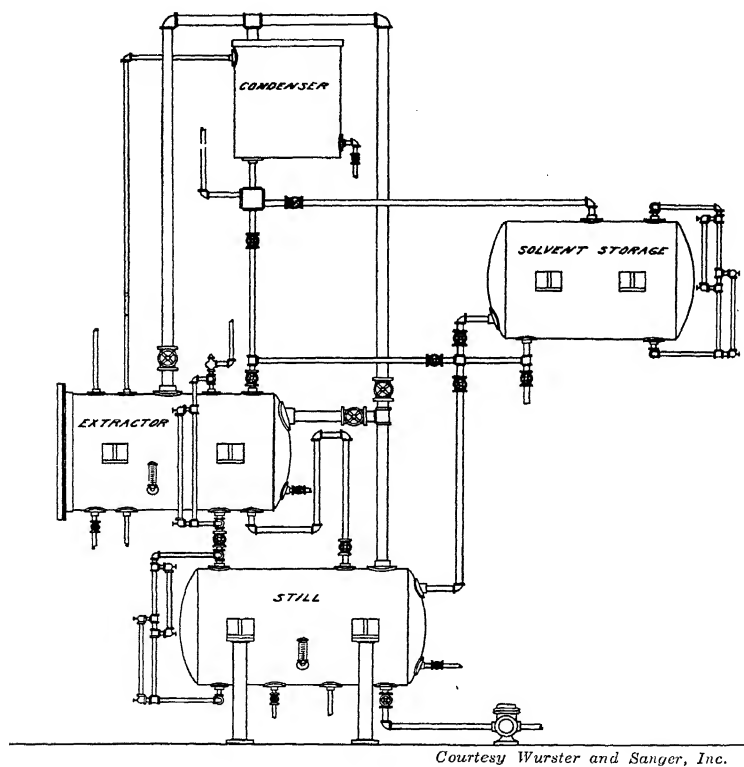
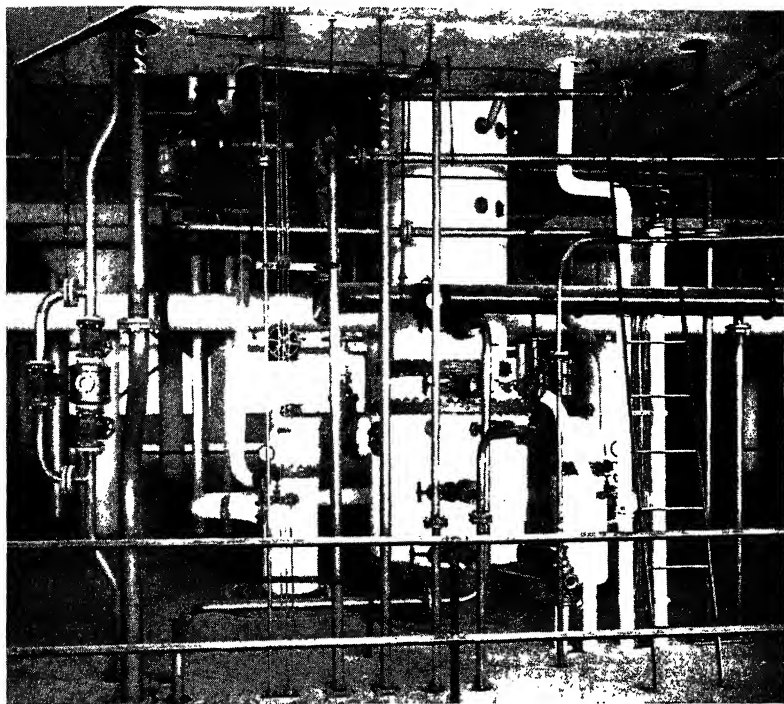


FIGURE 115. Stationary Solvent Extraction Plant.

tion of this equipment will be found in Chalmers, "Production and Treatment of Vegetable Oils," Van Nostrand, 1919.

Another illustration of the recovery of the solvent from oil extraction is given by the Wurster & Sanger system shown in Figures 113 and 114, the first figure

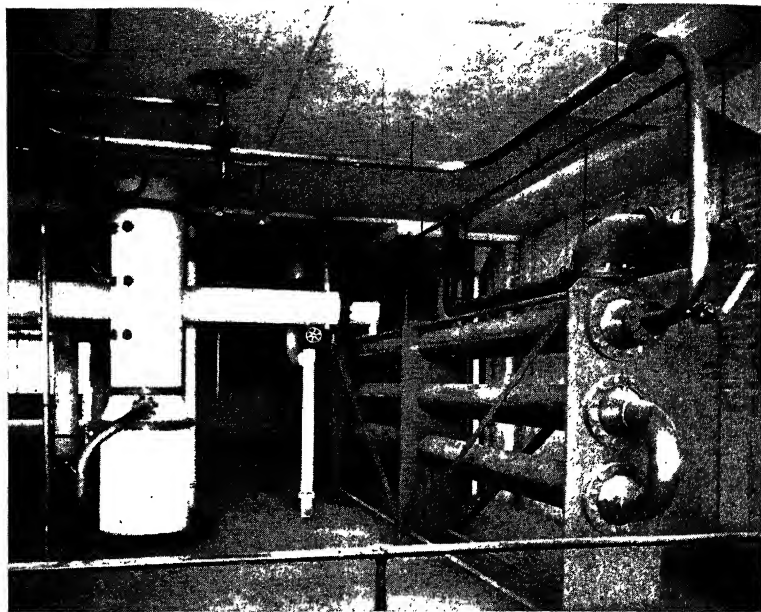


Courtesy Vulcan Copper & Supply Co.

FIG. 116. View of Furfural Recovery System.

showing the elevation of the system, and the second, the details of the extractor.

The extractor is a horizontal rotating drum fitted with both closed and open steam pipes. After the oil and solvent have been withdrawn from the drum to the still for separation, the residual solvent is volatilized by means of closed steam, the drum being under vacuum to keep the temperature down, and the last traces of solvent are afterward removed by open steam, this method decreasing the steam consumption for this part of the process, and improving the quality of the meal.



Courtesy Vulcan Copper & Supply Co.

FIG. 117. View of Furfural Recovery System.

Appendix

Table 1. Explosive Limits of Vapor-Air Mixtures at Room Temperature and Pressure (from U. S. Bureau of Mines, and Ullman).

Vapor concentration is expressed in per cent by volume.

Substance	Upper limit	Lower limit
Acetaldehyde, CH_3CHO	57.	4.
Acetone, $(\text{CH}_3)_2\text{CO}$	13.	2.3
Acetylene, C_2H_2	80.7	2.5
Ammonia, NH_3	27.	16.
Benzene, C_6H_6	8.	1.4
Benzine, petroleum,	5.	1.1
Butane, C_4H_{10}	8.5	1.9
Carbon disulfide, CS_2	50.	1.
Carbon monoxide, CO	73.	12.5
Dichloroethylene, $\text{C}_2\text{H}_2\text{Cl}_2$	13.	10.
Ethane, C_2H_6	12.5	3.2
Ethyl acetate, $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	11.5	2.2
Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$	19.	2.6
Ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$	48.	1.7
Ethyl formate, $\text{HCO}_2\text{C}_2\text{H}_5$	16.5	3.5
Ethyl nitrite, $\text{C}_2\text{H}_5\text{ONO}$		3.
Ethylene, C_2H_4	34.	3.3
Gasoline	6.0	1.4
Hexane, C_6H_{14}	6.5	1.8
Hydrogen, H_2	74.	4.1
Hydrogen sulfide, H_2S	46.	4.3
Illuminating gas	31.	5.3
Methane, CH_4	15.	5.0
Methyl acetate, $\text{CH}_3\text{CO}_2\text{CH}_3$	14.	4.1
Methyl alcohol, CH_3OH		6.0
Methylethyl ketone, $\text{CH}_3\text{COC}_2\text{H}_5$	12.	2.
Natural gas	13.5	4.8
Pentane, C_5H_{12}	8.0	1.4
Propane, C_3H_8	9.5	2.4
Pyridine, $\text{C}_6\text{H}_5\text{N}$	12.5	1.8
Toluene $\text{C}_6\text{H}_5\text{CH}_3$	7.0	1.3
Water gas, $(\text{CO}=\text{H}_2)$	72.	6.

Table 2. Vaporization Data

Name	Formula	Molecular weight	Latent heat of vaporization *	Heat of solution†
1. Acetaldehyde	CH_3CHO	44.	248	147
2. Acetone	$(\text{CH}_3)_2\text{CO}$	58.1	226	78
3. Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	93.1	196	39
4. Benzaldehyde	$\text{C}_6\text{H}_5\text{CHO}$	106.1	156	..
5. Benzene	C_6H_6	78.1	169	..
6. N-Butyl alcohol	$\text{C}_4\text{H}_9\text{OH}$	74.1	258	..
7. Carbon disulphide	CS_2	76.	153	..
8. Carbon tetrachloride	CCl_4	154.	83	..
9. Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	112.5	133	..
10. Chloroform	CHCl_3	119.4	106	..
11. <i>m</i> -Cresol	$\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$	108.1	181	..
12. <i>o</i> -Cresol	$\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$	108.1
13. <i>p</i> -Cresol	$\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$	108.1	...	45
14. Decane	$\text{C}_{10}\text{H}_{22}$	142.2	109	..
15. Diethyl acetate	$\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$	118.1
16. Do-decane	$\text{C}_{12}\text{H}_{26}$	170.2
17. Ethyl acetate	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	88.1	159	63
18. Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	46.1	375	98
19. Ethyl benzoate	$\text{C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_5$	150.1	116	..
20. Ethyl butyrate	$\text{C}_3\text{H}_7\text{CO}_2\text{C}_2\text{H}_5$	116.1	131	..
21. Ethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$	74.1	155	143
22. Ethyl propionate	$\text{C}_2\text{H}_5\text{CO}_2\text{C}_2\text{H}_5$	102.1	144	..
23. Heptane	C_7H_{16}	100.2	133	..
24. Hexane	C_6H_{14}	86.1	143	..
25. Isoamyl alcohol	$\text{C}_5\text{H}_{11}\text{OH}$	88.1	216	57
26. Isoamyl acetate	$\text{CH}_3\text{CO}_2\text{C}_5\text{H}_{11}$	130.1	120	..
27. Isobutyl acetate	$\text{CH}_3\text{CO}_2\text{C}_4\text{H}_9$	116.1	131	..
28. Isobutyl alcohol	$\text{C}_4\text{H}_9\text{OH}$	74.1	249	..
29. Methyl acetate	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	74.1	175	..
30. Methyl alcohol	CH_3OH	32.	472	112
31. Methyl butyrate	$\text{C}_3\text{H}_7\text{CO}_2\text{CH}_3$	102.1	143	..
32. Methyl isobutyrate	$\text{C}_3\text{H}_7\text{CO}_2\text{CH}_3$	102.1	135	..
33. Methyl isopropyl ketone	$\text{CH}_3\text{COC}_2\text{H}_5$	86.1	160	..
34. Methyl propionate	$\text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$	88.1	160	..
35. Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$	123.1	142	..
36. Nitrotoluene- <i>o</i> -	$\text{C}_6\text{H}_4(\text{CH}_3)\text{NO}_2$	137.1
37. Nonane	C_9H_{20}	128.2
38. Octane	C_8H_{18}	114.2	128	..
39. Phenol	$\text{C}_6\text{H}_5\text{OH}$	94.1	...	-6.
40. Propyl propionate	$\text{C}_2\text{H}_5\text{CO}_2\text{C}_3\text{H}_7$	116.2	130	..
41. Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	92.1	155	..
42. Water	H_2O	18.	965	..
43. <i>o</i> -Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	106.1	148	..
44. <i>m</i> -Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	106.1	147	..
45. <i>p</i> -Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	106.1	146	..

* *Latent Heat of Vaporization.* This heat effect is in B.t.u. per pound at the boiling temperature at 760 mm. pressure.

† *Heat of Solution.* This is the heat evolved in B.t.u. when one pound of the liquid is dissolved in a very large amount of water at room temperature. If a concentrated solution be produced instead of a very dilute one, the heat effect will be smaller than shown in the table. For a method for the calculation of this heat effect, see any textbook of Physical Chemistry.

for Various Solvents.

Boiling temperatures* in °C. at different pressures (in mm.)							Specific gravity †	
760	100	50	30	20	10	5		
20.8	0.80	1.
56.6	0.797	2.
183.9	119.4	101.9	90.9	82.8	69.2	57.9	1.022	3.
178.3	112.5	95.3	83.5	75.2	62.0	50.1	1.046	4.
80.2	25.8	11.6	1.8	-4.3	-13.6	-22.1	0.879	5.
117.6	69.8	56.9	48.0	41.5	31.0	21.7	0.824	6.
46.0	-5.8	-18.0	-23.7	-26.5	-29.4	1.292	7.
76.8	22.1	7.6	-2.2	-9.2	-32.5	1.63	8.
131.8	70.4	53.7	42.7	34.5	21.8	10.4	1.112	9.
61.2	1.526	10.
200.5	138.0	120.8	109.5	101.3	87.8	76.0	1.033	11.
190.1	127.4	110.3	98.9	90.6	77.6	65.5	1.039	12.
201.1	138.4	121.3	110.1	101.8	88.6	76.5	1.033	13.
173.0	107.0	90.0	78.0	68.0	55.0	14.
102.2	47.3	32.8	25.0	20.2	15.
214.5	145.5	126.0	113.8	103.0	88.0	0.766	16.
77.2	25.9	12.4	3.1	-3.8	-14.2	-23.9	0.924	17.
78.2	33.9	21.8	12.9	6.3	-4.3	-14.7	0.736	18.
213.4	86.0	1.066	19.
119.9	62.6	46.1	1.036	20.
34.6	-11.1	-24.0	0.73	21.
99.0	44.9	30.8	21.1	13.6	2.1	-7.8	22.
98.4	41.6	26.4	16.3	9.5	-2.1	0.712	23.
69.0	15.6	1.5	-7.9	-15.0	-25.7	-34.1	0.663	24.
130.1	80.7	66.9	58.4	51.5	40.3	30.2	0.824	25.
148.0	0.857	26.
116.3	59.7	43.7	27.
107.9	61.7	47.3	40.2	33.9	21.2	11.1	0.803	28.
57.1	8.9	-4.5	0.95	29.
64.7	20.6	8.1	0.2	-6.8	-16.5	-25.0	0.78	30.
102.8	48.0	33.0	23.2	15.6	4.2	-6.1	1.029	31.
92.3	38.8	24.2	14.6	7.7	-3.6	-13.8	32.
88.9	32.1	23.2	17.9	11.9	33.
79.7	28.1	14.1	4.8	-1.8	-12.6	-22.3	34.
208.3	139.9	120.2	108.2	99.1	85.4	72.9	1.20	35.
220.4	150.6	131.7	119.2	109.6	94.8	81.8	1.163	36.
149.5	86.0	70.0	59.0	49.0	38.0	0.733	37.
125.8	65.6	50.2	39.3	31.3	19.1	7.7	0.708	38.
181.4	120.2	104.7	93.8	85.8	73.5	62.5	1.08	39.
122.2	65.1	48.0	40.
110.4	51.8	36.3	25.5	17.9	6.0	0.882	41.
100.0	51.7	38.3	29.9	22.3	11.4	1.3	1.00	42.
144.0	81.2	64.1	52.6	44.5	0.756	43.
139.2	76.9	60.2	49.1	30.0	0.878	44.
138.9	76.4	59.5	48.0	0.862	45.

* *Boiling Temperature.* This table shows the temperature in °C. at which the pure substance in question will boil when under the external pressure at the head of the column.

† *Specific Gravity.* Specific gravity is given at room temperature. For more accurate data see Landolt-Börnstein Chemische Physikalische Tabellen and the International Critical Table.

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